ARS ORIENTALIS

THE ARTS OF ISLAM AND THE EAST

1817

This volume is dedicated to the memory of Rutherford John Gettens

VOL. 11 1979
FREER GALLERY OF ART, SMITHSONIAN INSTITUTION
DEPARTMENT OF THE HISTORY OF ART,
UNIVERSITY OF MICHIGAN

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Published with the aid of grants from John Thacher, Washington D.C., and the JDR 3rd Fund.

Composed by Syntax International and printed by the Maple-Vail Book Manufacturing Group,
York, Pennsylvania.

Library of Congress Catalog Card No. 54-14692

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FOREWORD

This volume of *Ars Orientalis* is dedicated to the memory of Rutherford John Gettens (1900–1974).* It differs from past volumes in being composed entirely of contributions to the technical study and conservation of works of art and archaeological materials from the oriental world, along with related historical studies. This was the field to which John Gettens himself contributed so much when in 1951 he started, then directed, and, after his retirement in 1968, continued research in the Freer Gallery's Technical Laboratory, though we should not forget that his work, taken over the whole of a career going back before 1930, was not confined to the arts of Asia. There are all too few places to publish studies of the kind presented here. In collecting together original contributions to technical studies of oriental art, we hope to have accomplished a task that well serves Gettens' memory.

A number of the authors here represented were John Gettens' friends and professional colleagues, and several of them have supplied personal notes, which follow later. It is fascinating to see, however, the number of papers here that owe something to the past work of Gettens himself, and, in some cases, that are direct continuation of his own studies. Notable examples of the latter are the articles by Elisabeth West FitzHugh, and by W. T. Chase and Ursula Martius Franklin.

The Chase and Franklin paper contains an account of the previous investigations of black-surfaced mirrors, in which the name of Gettens figures so largely. Chase worked with Gettens on the question of acid-etched bronze inscriptions during the middle 1960's; it is pleasing to be able to expand here on some ideas which arose at that time. In 1961, Franklin presented a paper on black-surfaced mirrors at the Freer Bronze Symposium, which began an extended, helpful, and stimulating exchange of ideas on the subject with Gettens. The present paper, intended as a tribute to Gettens, can only in a very small way attest to his continued encouragement and kind support. It also echoes Gettens' statement on the findings in the *Freer Chinese Bronzes*, Volume II (p. 31), "They are sure to raise more questions than they answer, but that is as it should be."

FitzHugh's contribution is a continuation of ideas presented by Gettens in a paper, "Japanese Paintings: Technical Studies and Conservation at the Freer Gallery of Art," delivered by him to the Lisbon Congress of the International Institute for Conservation in 1972. The technical examination of *Ukiyo-e* painting in the Freer's collection was begun by Gettens and FitzHugh in 1969. They intended that the study would form part of a catalogue in which the paintings would be discussed as examples in the history of technology as well as from their art-historical aspect. In the present volume, FitzHugh reports on the pigment identification aspect of the survey of the paintings, thus continuing many years of reporting on pigment occurrences on Oriental works of art, begun with three articles by Gettens in *Technical Studies* in 1938 on wall paintings in Chinese Turkestan, Afghanistan and central China.

The above paper to the Lisbon Congress also discussed the conservation of Japanese paintings, and in particular the "panel" technique for mounting them. Here Kenzō

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* For an obituary and full bibliography see *Ars Orientalis*, vol. 10 (1975), pp. 195–205.

Toishi uses this as a starting point for his discussion of the mechanics of Japanese paintings mounted as scrolls.

John Gettens' first published paper dealt with the restoration of bronzes from Iraq; it signalled the beginning of a lifetime interest in ancient bronzes, their fabrication, corrosion and treatment. The catalogue of the Chinese bronze ceremonial vessels in the Freer Gallery (*The Freer Chinese Bronzes*) represents the culmination of this aspect of his work. Barbara Keyser's paper on the fabrication of the two bronze *chien*, one in the Freer Gallery, the other in the Minneapolis Institute of Arts, provides additional discussion and detail concerning the problem of decor replication in the late Chou period.

In fact, fully a third of the contributions to this volume deal with bronze objects of one kind or another; and we should also note the coincidence between Li Chung's investigation of an iron-bladed bronze axe and the paper, "Two early Chinese bronze weapons with meteoritic iron blades," by Gettens, Clarke and Chase (*Freer Gallery Occasional Papers*, 1971, vol. 4, no. 1).

The two papers by Donald Gibbons and his co-workers on objects in silver recall the article by Gettens and Claude L. Waring in *Ars Orientalis* Vol. 2 (1957) on the spectrographic analysis of ancient Near Eastern silver. The one by James Watt recalls Gettens' long-standing interest in cobalt. His unpublished manuscript "On the early use of smalt as a paint pigment and its possible asiatic origin" was prepared in the 1950's and put aside when the study of the Chinese ceremonial bronzes in the Freer was begun.

In presenting their results on lead isotope ratios from China and Japan, Robert Brill and his co-authors have noted that the first lead isotope determination on a Far Eastern object was on a specimen supplied by John Gettens. Brill says, "Because he was much admired by the authors of this paper, as well as being a close friend to some of us, we are especially pleased to dedicate this paper to him."

This feeling of dedicating a piece of work to the memory of an old friend is one that has been expressed by several authors, and we can do no better than close with notes provided by three of them. Kazuo Yamasaki shared Gettens' long-standing interest in the history of pigments, and states that the paper by him and Yoshimichi Emoto, "is dedicated to the memory of Rutherford John Gettens. His name became familiar to Japan through the book, R. J. Gettens and G. L. Stout, *Painting Materials, A Short Encyclopaedia*, 1942, a copy of which was brought to Japan by Stout when he served as the Chief, Arts and Monuments Section, General Headquarters of the Occupation Forces. Stout gave this book to Ōoka, Director of the Repair Office of the Hōryūji Temple, and one of the present authors (K. Y.) borrowed this book from him, and found it very interesting and useful. Yamasaki sent a letter to Gettens when correspondence between Japan and the U.S.A. became possible, and it took several years before Gettens and Yamasaki met for the first time in 1956 in Washington, D.C. After that they collaborated in various projects such as the publication of the Freer Technical Abstracts, studies on Chinese bronzes, and those on the pigments used in Japanese paintings. The work of Rutherford John Gettens is to be remembered forever by those working in these fields."

Professor Caley provided the following note on his paper: "The article by Earle R. Caley, In Soon Moon Chang, and Nilufer Paranyi Woods may be said to have had its beginning late in 1956, when John Gettens discussed with Earle R. Caley the need for more information on the exact chemical composition of ancient Chinese alloys. At that time Professor Caley agreed to supervise or undertake the analysis at the Ohio State University of any metal objects or fragments that John Gettens could supply from the Freer Gallery. The result of this discussion and agreement was that John Gettens sent to Professor Caley for analysis fourteen specimens very early in 1957. In that same year Mrs. Chang, a graduate student in chemistry at Ohio State, analyzed by gravimetric methods a number of samples prepared from these specimens, and in 1962 Mrs. Woods, also a graduate student, analyzed other samples by spectrography. The publication of the results of both sets of analyses was delayed in the hope of finding other graduate students interested in the analysis of additional specimens to be supplied by John Gettens. This hope was never realized and no attempt was made at the time to publish what had been done. In a way this long delay in publication is rather fortunate, for the results of the analyses of the specimens supplied by John Gettens over 20 years ago now appropriately appear in this memorial volume."

Finally, concerning the paper by Elaine Savage and Cyril Stanley Smith, the authors say: "It is especially gratifying to have this paper appear in a volume dedicated to the memory of the late John Gettens. For one of us (C.S.S.) the inspiration of contact with him began in the shared experience of wartime Los Alamos. Personal and professional friendship continued to deepen as Gettens' work at the Fogg and the Freer made it ever more clear that the history of technology could not be written without the enjoyment of works of art or attention to the new types of study that were being done in museum laboratories under his leadership and that of a very few colleagues."

ACKNOWLEDGMENTS

The Editors wish to thank the following members of the Freer Galley staff for their help in preparing this volume: Ann Yonemura and Hin-cheung Lovell for checking romanizations and other details of oriental scholarship; James T. Hayden for the preparation of photographs, and Stephanie Faul for retyping several of the manuscripts.

ABSTRACTS

Kazuo Yamasaki, Yoshimichi Emoto, Pigments Used in Japanese Paintings from the Protohistoric Period through the 19th Century. *Ars Orientalis*, Vol. 11 (1979), pp. 1–14.

Pigments used in Japanese tombs from the fifth to the seventh centuries are exemplified by those found in the Ōtsuka and the Torazuka tombs. Notable paintings from the seventh–eighth centuries are those in the Takamatsuzuka tombs and the Hōryūji Temple. Some forty architectural interior paintings and decorations from the Nara period (643–693) through the Muromachi period (1393–1573) have been studied for pigment occurrences and the results are presented here. The chief changes in use were the replacement of white clay by powdered oyster shell in the fifteenth–sixteenth centuries and the temporary replacement of azurite by indigo around the ninth-eleventh centuries. In the Shōsōin repository are various handicrafts and paintings from the 8th century; pigment occurrences on some of these are presented. Also in the Shōsōin are pigment samples of red lead, powdered silver and lead white, and some results are available from studies on these. Results from early handscrolls and from 17th century paintings are given briefly.

Kenzō Toishi, The Scroll Painting. *Ars Orientalis*, Vol. 11 (1979), pp. 15–25.

The paint layer in a Japanese painting has a generally porous structure; an appropriate mathematical model based on an array of uniform close-packed spheres suggests that the glue medium covers only about half of the surface area of the pigment grains. Mounting the painting as a scroll keeps such a paint layer protected, makes the painting very compact while the scroll is rolled for storage, and avoids the chance of large stresses developing from humidity changes. When a scroll is unrolled and displayed, certain deformations, characterized as first-stage and second-stage deformation, may be observed. Deterioration of the materials results in embrittlement, which leads to the formation of lateral cracks and creases. Other kinds of damage result from careless handling, tieing the rolled scroll too tightly, or take the form of flaking of the paint layer. The recommended maximum period of exhibition of a scroll is about one month. The recommended relative humidity is 55–60%; below 50% should be avoided.

Elisabeth West FitzHugh, A Pigment Census of Japanese *Ukiyo-e* Paintings in the Freer Gallery of Art. *Ars Orientalis*, Vol. 11 (1979), pp. 27–38.

Pigment occurrences on 151 paintings of the *Ukiyo-e* school are presented. The paintings are attributed to five dating groups: late 16th to mid-17th century, mid-17th to mid-18th century, 2nd quarter to end 18th century, 2nd quarter 18th to 1st quarter 19th century, end 18th to late 19th century. Pigment identification was by optical microscopy, microchemistry and X-ray diffraction; the morphological and optical characteristics of, and the chemical tests used to identify, the eighteen pigments found are described. The pattern of occurrences over the five dating groups is summarized.

Steven Weintraub, Kanya Tsujimoto, Sadae Walters, *Urushi* and Conservation: The Use of Japanese Lacquer in the Restoration of Japanese Art. *Ars Orientalis*, Vol. 11 (1979), pp. 39–62.

For centuries, *urushi* (Japanese lacquer), a natural secretion of *Rhus vernicifera*, has been used in Japan, not only for creating works of art, but also for the preservation and repair of artifacts. *Urushi* is outstanding for its hardness, resistance to weathering and water damage, and adhesive properties, but it is expensive and it causes dermatitis in the artisan. The procedure for creating a lacquer object as well as the possible damage it may suffer are described. The same techniques are used when *urushi* is used to repair lacquer, wooden sculpture, architecture and ceramics. Examples of lacquer repairs to lacquer, three types of wooden sculptures, and ceramics are illustrated. Today, *urushi* is often replaced by synthetic materials which are lower in cost and easier to apply.

James C. Y. Watt, Notes on the Use of Cobalt in Later Chinese Ceramics. *Ars Orientalis*, Vol. 11 (1979), pp. 63–85.

The first part of the paper discusses the identity, origin and impurities of the cobalt ores used as the coloring agent in Chinese blue and white porcelain dating from the fourteenth to the present century. Both Western and modern Chinese sources and analyses are cited. The second part contains the author's translations, comments and annotations to early Chinese texts relevant to cobalt blue. The author concludes that cobalt importation began in the fifteenth century but ceased around the seventeenth century and resumed in the twentieth century. During the eighteenth and nineteenth centuries local ores were used.

Robert H. Brill, Kazuo Yamasaki, I. Lynus Barnes, K.J.R. Rosman, Migdalia Diaz, Lead Isotopes in Some Japanese and Chinese Glasses. *Ars Orientalis*, Vol. 11 (1979), pp. 87–109.

Spectroscopic and chemical analyses, for the most part previously published, are given for 23 Chinese and Japanese glasses. Lead isotope ratios are presented for 40 samples of glass, metallic lead, pigments and ores. It is shown that these data are useful for classifying East Asian glasses. A clearly-defined 'Nara' type of lead has emerged, which falls within the range of isotope ratios found for Japanese lead ores. Other glasses from Japan, differing considerably from the Nara type, are believed, in at least some cases, to be of Chinese origin. Early Chinese glasses yield lead isotope ratios of two markedly different types. There is only a partial correlation for Chinese glass between isotope ratio and barium oxide content.

Jay D. Frierman, Frank Asaro, Helen V. Michel, The Provenance of Early Islamic Lustre Wares. *Ars Orientalis*, Vol. 11 (1979), pp. 111–126.

Islamic pottery decorated with overglaze lustre dates from the ninth century. The place of manufacture of the early pieces and the spread of the manufacturing technique are problems that are approached here by chemical fingerprinting using neutron activation analysis. Fingerprinting is based on the concentrations of 18 to 20 elements. Nine earthenware potsherds of the 9th–11th centuries and seven faience sherds of the 11th–13th centuries were investigated. The results make it likely that the Egyptian and Iranian 9th–10th century earthenware sherds have an Iraqi origin. The comparisons are less definite for the faience samples; the synthetic faience bodies form groups whose compositions are not as homogeneous as for pottery. However the work suggests that by the end of the 12th century lustre painting was being done in Egypt, Syria, Iraq and Iran.

Barbara W. Keyser, Decor Replication in Two Late Chou Bronze *Chien*. *Ars Orientalis*, Vol. 11 (1979), pp. 127–162.

Two bronze *chien* basins were studied to reconstruct replication techniques of late Chou founders. Ancient foundry techniques are reviewed. Both *chien* were examined by microscopy, radiography, chemical analysis and UV illumination to reveal condition and method of manufacture. Mold marks, casting remnants, chaplets, handles, decor and inscriptions are compared. The decor is modular; six basic motifs are repeated to produce the total design. However, two separate but similar vessel molds were constructed for casting the two vessels. Excavations at Hou-ma, where both *chien* may have been fabricated, provide information as to how appendages and decor motifs were replicated.

Donald F. Gibbons, Katharine C. Ruhl, Dorothy G. Shepherd, Techniques of Silver-smithing in the Hormizd II Plate. *Ars Orientalis*, Vol. 11 (1979), pp. 163–176.

Techniques of silversmithing in the Sasanian Hormizd II plate were examined using microscopy, radiography, metallography, electron beam microprobe and X-ray fluorescence. Results show that the plate was made from a silver sheet hammered from an ingot, that relief was created by removing metal from the background, that chasing was used for fine lines, and that sixteen separate inserts form the high relief. The foot was applied by soldering. Mercury gilding was applied selectively.

Donald F. Gibbons, Katharine C. Ruhl, The Metallurgical Technique of the Silver 'Plate with Figures', Gupta Period. *Ars Orientalis*, Vol. 11 (1979), pp. 177–182.

A silver plate with figures was examined by microscopy, radiography and metallography. The alloy composition of Ag 55%, Cu 45% forms a structure of copper-rich dendrites in a silver-rich matrix. The plate was hammered out from a cast slug. Chemical treatment of the surface depleted the copper-rich phase, leaving a layer of silver. Relief decoration was developed by selectively removing the silver layer. Burnishing consolidated the spongy silver. A foot was soldered on; the background was gilded.

Earle R. Caley, In Soon Moon Chang, Nilufer Paranyi Woods, Gravimetric and Spectrographic Analysis of some Ancient Chinese Copper Alloys. *Ars Orientalis*, Vol. 11 (1979), pp. 183–193.

Fourteen specimens of Chinese bronze from the Chou and Han dynasties have been analyzed gravimetrically (for major elements), by emission spectrography (for minor elements) and volumetrically (in two cases, for antimony). The accuracy of the results is discussed. The alloys vary a good deal, copper-tin (including high-tin) bronzes, leaded high-tin bronzes and copper-lead alloys with some tin all being found. The major component results are compared with those from Gettens and from Chikashige. Results on minor components are compared with those from Gettens.

Masaaki Sawada, Non-destructive X-ray Fluorescence Analysis of Ancient Bronze Mirrors Excavated in Japan, *Ars Orientalis*, Vol. 11 (1979), pp. 195–213.

Over 2500 bronze mirrors made either in China or Japan have been excavated from Japanese tombs of the Yayoi and Tumulus periods. Chinese mirrors differ from the Japanese ones in style, manufacturing techniques, and composition (Chinese: 60–75% Cu, 17–30% Sn, and 3–7% Pb; Japanese: 70–90% Cu, 2–20% Sn, and 3–8% Pb). In an attempt to distinguish the two types by analysis without sampling, Sn/Pb ratios were determined by analyzing 1.5 cm spots on the surface with X-ray fluorescence. Results correlate well with those from wet analysis and those previously reported. While the two groups overlap where the ratio Sn/Pb is about 2.0–3.0, the provenance of about 80% of the mirrors can be quite reliably distinguished.

W. T. Chase, Ursula Martius Franklin, Early Chinese Black Mirrors and Pattern-etched Weapons. *Ars Orientalis*, Vol. 11 (1979), pp. 215–258.

The black patina on Chinese bronze mirrors was studied by microscopy, metallography, hardness, density measurements, electron microprobe, X-ray fluorescence and X-ray diffraction. A prototypical black mirror is described: 70% Cu, 25% Sn, 5% Pb, in the as-cast state, lightly polished, the surface "sealed" to give a non-metallic surface—possibly an amorphous silicate—and a gradual transition from the non-metallic layer, through an altered layer to the bronze. Geographical and chronological limits of black mirrors are described. Material and documentary evidence for the original color of the mirrors is offered. Pattern-etched weapons are described and illustrated as comparative and related artifacts. Modern Chinese technical studies of the problem are reviewed. Possible techniques of surface treatment are suggested.

Li Chung, Studies on the Iron Blade of a Shang Dynasty Bronze *Yüeh*-axe unearthed at Kao-ch'eng, Hopei, China. *Ars Orientalis* Vol. 11 (1979), pp. 259–290. (Translation of an article published in *Kaogu Xuebao*, 1976, No. 2 (No. 45 in overall sequence), (pp. 17–34).

The axe, dating from the 14th century B.C., consists of the completely corroded tang of the iron blade embedded in a bronze handle. The oxidized iron contains 2.5% NiO and 0.24% CoO. Metallographic and electron microprobe investigations revealed few silicate inclusions, which man-made iron usually contains. The electron microprobe also demonstrated the lamellar nature of nickel and cobalt distribution; although nickel and cobalt are believed to have been preferentially lost during corrosion, the lamellar distribution can only be explained by an extremely slow cooling process. This affords conclusive evidence that the iron was of meteoritic origin. Certain other particles seen in the sections were shown to be minerals deposited, probably, from ground water.

Elaine I. Savage, Cyril Stanley Smith, The Techniques of the Japanese Tsuba-maker. *Ars Orientalis*, Vol. 11 (1979), pp. 291–328.

Japanese metalworking techniques for making tsuba (sword-guards) were studied by microscopy and metallography. Chemical analysis of ferrous and non-ferrous tsuba confirmed alloy compositions already in the literature. The microstructure of two iron, two brass and one *shibuichi* tsuba is described and illustrated. Carving, inlay, and gilding techniques are explained. Layered metal tsuba were also examined and the technique is discussed. Surface textures were produced mechanically or by chemical etching. The final treatment was patination, modified by polishing, heating, or organic coatings.

ARS ORIENTALIS

Rutherford John Gettens (1900–1974)

PIGMENTS USED ON JAPANESE PAINTINGS FROM THE PROTOHISTORIC PERIOD THROUGH THE 17th CENTURY

By KAZUO YAMASAKI*
and YOSHIMICHI EMOTO**

INTRODUCTION

The first chemical study on pigments used in old paintings of Japan was probably that on the wall painting of the Hōryūji temple near Nara carried out in 1919 by Masumi Chikashige,[1] professor of inorganic chemistry at Kyōto University, who was also a pioneer in the chemical analysis of Chinese bronzes. Rokurō Uemura studied the coloring materials in the paintings and textiles from sources found in Japanese literature, and gave chemical interpretations.[2] An extensive historical study in the same field, especially on dyes, was made by Yukichika Maeda.[3]

In this article studies of the pigments used on Japanese paintings from the protohistoric period through the 17th century, the early Edo period, will be presented. The methods of investigation included microchemical and spectrochemical analyses, infrared photography, X-ray diffraction and radiography, and X-ray fluorescence spectroscopy.

PROTOHISTORIC DECORATED TOMBS

The early cultural periods in Japan are divided into two, the Jōmon and the Yayoi periods, named after the respective types of pottery excavated. The former lasted until about the third century B.C. When it began is not yet certain, but a duration of several thousand years has been claimed by radiocarbon dating. The Yayoi period lasted from about the third century B.C. to about the third century A.D. From these two periods, however, no pictorial art in color is known, except for some pottery painted with red ochre or cinnabar. After the Yayoi period came a protohistoric period when huge mounds were constructed for the burial of the dead. It is thus called the Kofun period (Tumulus period) and lasted from about the third century to the end of the seventh century. The duration of the Tumulus period varies somewhat between the western part and the central part of Japan. The end of the Tumulus period overlaps the historic Asuka-Nara period (552–793 A.D.) without clear demarcation.

Some of the tombs of the fifth–seventh centuries in the tumulus period have underground funerary chambers decorated with paintings. Most of these tombs exist in the northern part of Kyūshū, i.e. Fukuoka and

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[1] *Hōryūji Hekiga Hozon Hōhō Chōsa Hōkoku* (Report on the Conservation of Wall Painting of the Hōryūji temple). (Tokyo: Ministry of Education, 1920. Reprinted in 1939).

[2] Rokurō Uemura, *Tōhō Senshoku Bunka no Kenkyū* (Studies on the dyeing culture in the East). (Tokyo: Dai-ichi Shobō, 1933).

[3] Yukichika Maeda. *Nihon Shikisai Bunka Shi* (Cultural History of Colors in Japan) (Tokyo: Iwanami Shoten, 1960).

Kumamoto prefectures, but in recent years more decorated tombs have been found in Kyūshū as well as in the central and eastern parts of the main island, Honshū. As of 1974, the total number of tombs decorated with colors amounted to 95, with 36 in Fukuoka, 4 in Saga, 31 in Kumamoto, 8 in Ōita, 1 in Hyōgo, 1 in Wakayama, 3 in Kanagawa, 3 in Ibaraki, 4 in Fukushima and 4 in Miyagi prefectures.[4]

In 1949–1950 Yamasaki[5] examined pigments from about forty of these tombs including all the important ones in Kumamoto and Fukuoka prefectures that had been studied archaeologically. Most of the tombs have only simple decorations such as concentric circles or triangles painted in red alone, but some have figures such as men, horses, birds, and boats in addition to geometric designs. The most gorgeously decorated tomb in Japan is the Ōtsuka tomb (king's tomb) in Fukuoka prefecture.[6] All the walls of the funerary chamber were covered with paintings representing horses, men, quivers and swords, triangles and mysterious geometrical figures. Five colors are used: white, red, yellow, green, and black. The pigments of this Ōtsuka tomb were studied again in 1969 by Emoto by X-ray diffraction as part of the conservation work.[7] These results are listed in Table 1.

Table 1

Pigments Used in the Ōtsuka Tomb (mid-6th Century)

Color	Pigments
white	clay (sericite?)*
red	impure red ochre (α-Fe_2O_3)*
yellow	impure yellow ochre (α-quartz, orthoclase and sericite)*
green	powdered green rock (glauconite)*
black	black mineral containing iron and manganese (amorphous manganese mineral)*

* Minerals shown in the parentheses were identified mainly by X-ray diffraction (see footnote 7).

A survey of the pigments used in other decorated tombs in Kyūshū showed that the kinds of pigments were almost the same as in Table 1. In addition carbon was used as a black pigment. Only coloring materials found near the tombs were used, and no pigments such as azurite, malachite, and cinnabar were found. Probably the use of such bright colored minerals was not known in Kyūshū at that time. As an example of a decorated tomb situated in the eastern part of Japan the early seventh century painting of the Torazuka tomb, Ibaraki prefecture, is shown in Figure 1. The figures are painted with red

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[4] Shigetaka Otomasu (editor). *Sōshoku Kofun to Monyō* (Decorated Tomb and Patterns), Vol. 8 of *Kodaishi Hakkutsu* (Discovery of Ancient History). (Tokyo: Kōdansha, 1974), pp. 152–160.

[5] Kazuo Yamasaki, "*Sōshoku Kofun no Ganryō no Kagakuteki Kenkyū* (Chemical Studies on the Pigments of Ancient Decorated Tombs in Japan)." *Kobunkazai no Kagaku* (Scientific Papers on Japanese Antiques and Art Crafts), no. 2(1951), p. 8; *idem.*, "Technical Studies on the Ancient Art Objects in Japan, with Special Reference to the Treasures Preserved in the Shōsōin", *Application of Science in Examination of Works of Art, Proceedings of the Seminar, 1965* (Boston: Museum of Fine Arts, 1967), pp. 114–125 and Figure 18; *idem.*, "Pigments employed in Old Paintings of Japan". *Archaeological Chemistry, A symposium*. Martin Levey (Editor). (Philadelphia: University of Pennsylvania Press, 1967), pp. 347–365, Figure 3.

[6] Sueji Umehara and Yukio Kobayashi, "*Chikuzen no Kuni Kaho-gun Ōtsuka Sōshoku Kofun* (Ōtsuka Decorated Tomb, Kaho County, Chikuzen Province)", *Report on Archaeological Research in the Department of Literature, Kyōto Imperial University*, vol. 15 (Kyōto: Kyōto Imperial University, 1939).

[7] Yoshimichi Emoto, "*Ōtsuka Kofun no Hozon* (Conservation of the Ōtsuka Tomb)", *Report on the Conservation of Decorated Tombs* (Fukuoka Prefectural Office, 1975).

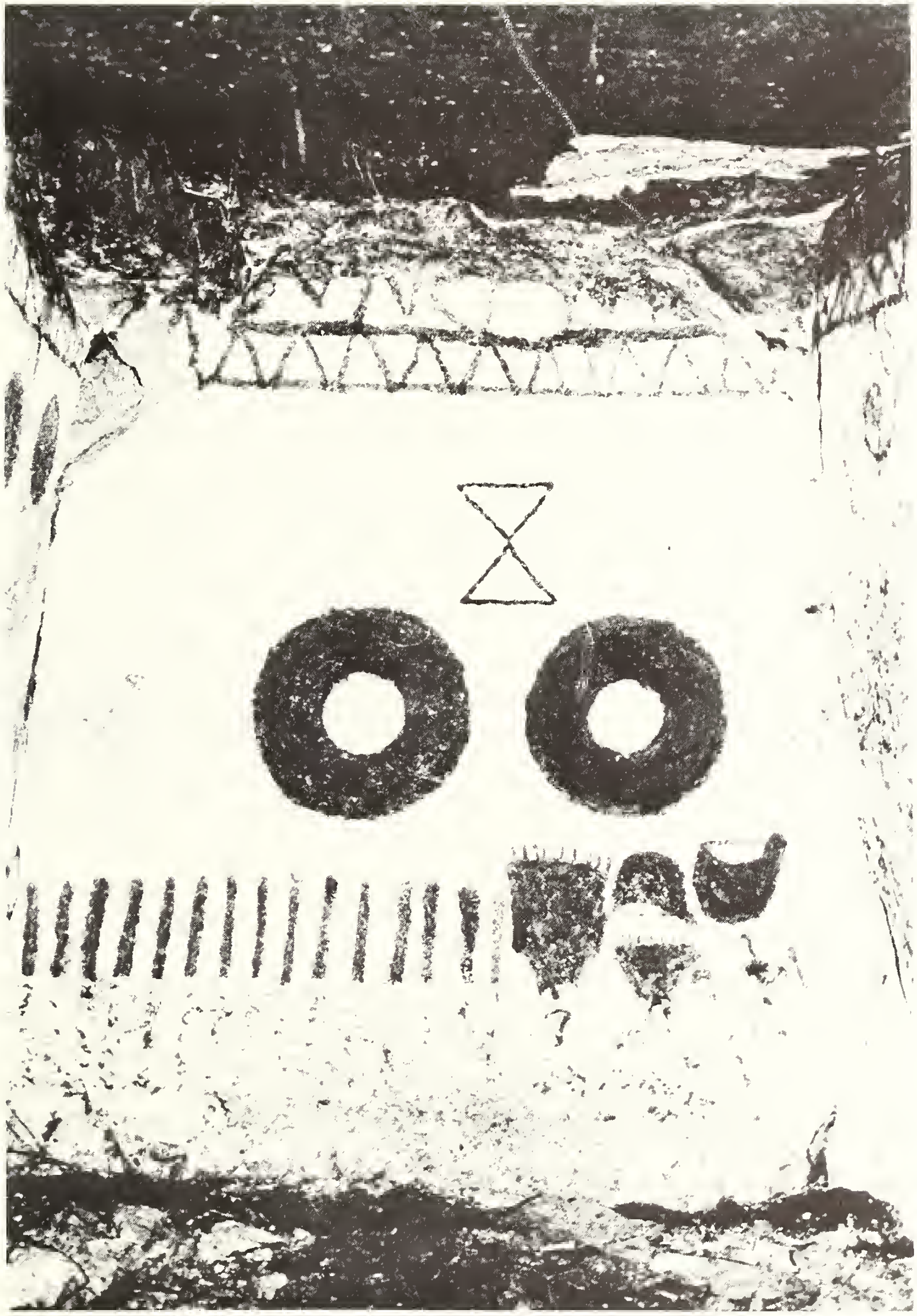

FIG. 1.—The inside view of the Torazuka tomb, Katsuta, Ibaraki prefecture, just after opening of the entrance. Figures are painted in red on the ground coating of clay.

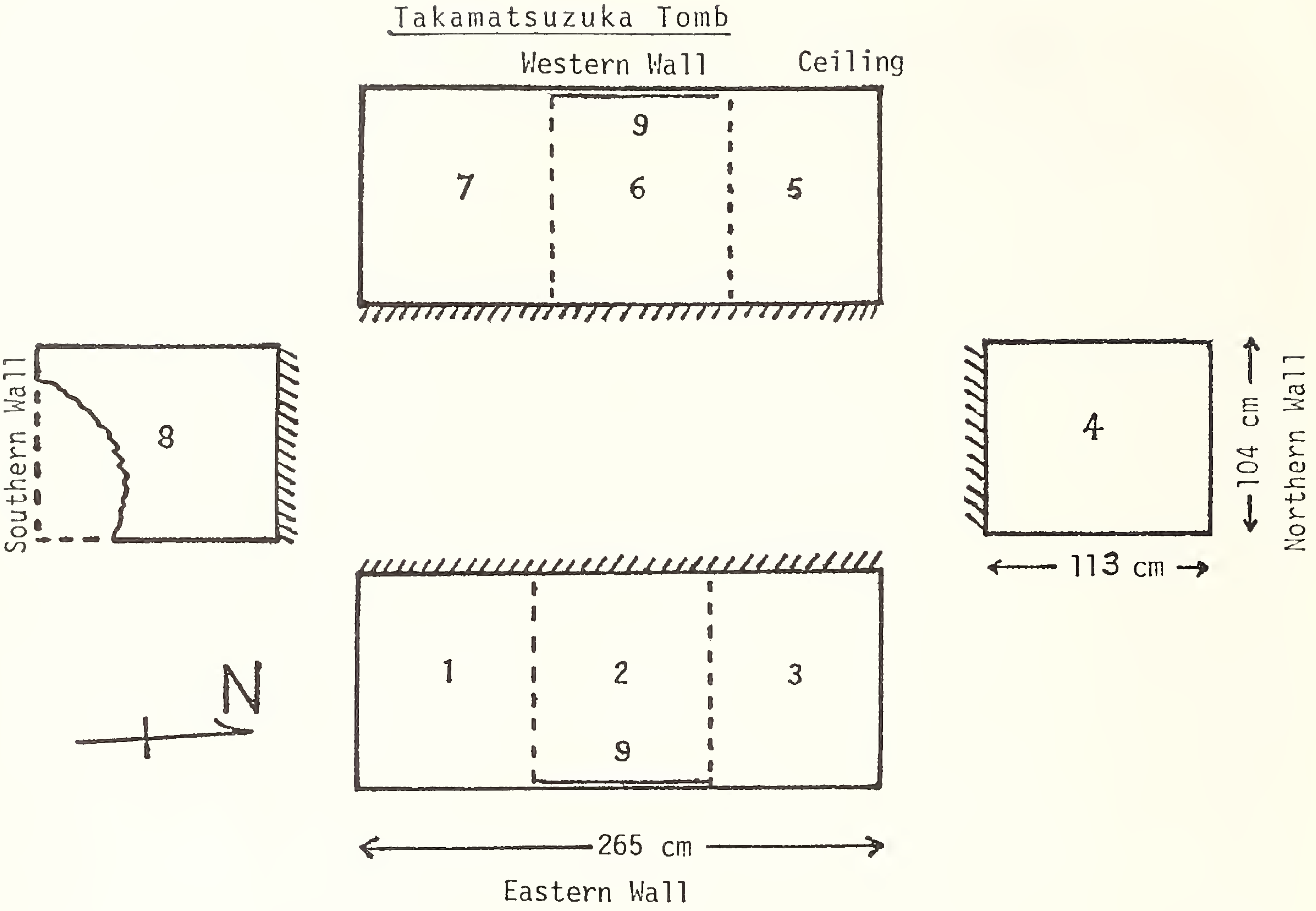

FIG. 2.—Positions of the painting in the Takamatsuzuka tomb. Eastern wall, 1) southern panel (four men), 2) middle panel (Blue Dragon), and 3) northern panel (four women). 4) Northern wall (Serpent-tortoise). Western wall, 5) northern panel (four women), 6) middle panel (White Tiger), and 7) southern panel (four men). 8) Southern wall (no painting remained). 9) The position of the ceiling where a celestial constellation is painted. The broken lines indicate the joints of the slabs.

ochre over a white ground coating, which Emoto identified by X-ray diffraction as α-Fe_2O_3, and a mixture of kaolinite, α-quartz and feldspar respectively.[8]

No information on the adhesives used in the paintings of decorated tombs is available because of the difficulty of obtaining sufficient amounts of samples for investigation.

A DECORATED TOMB OF THE NARA PERIOD

In March 1972 a small tomb named Takamatsuzuka in Asuka village, Nara prefecture, was excavated. It was a circular mound, 5 m in height and 18 m in diameter. The inner surfaces of the funerary chamber, including the ceiling and the floor, are coated with a thin layer of lime plaster (2–7 mm thick), and series of non-Buddhistic figures are painted on the side walls, with a celestial

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[8] Yoshimichi Emoto, unpublished data. An official report on the Torazuka tomb will be published in 1978.

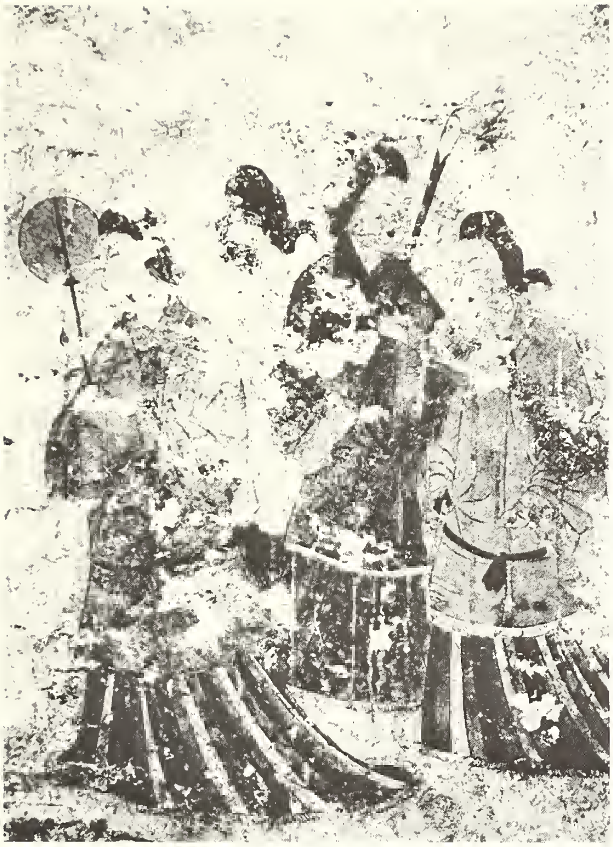

FIG. 3.—Four women in the northern panel of the Western wall of the Takamatsuzuka tomb, × 0.15

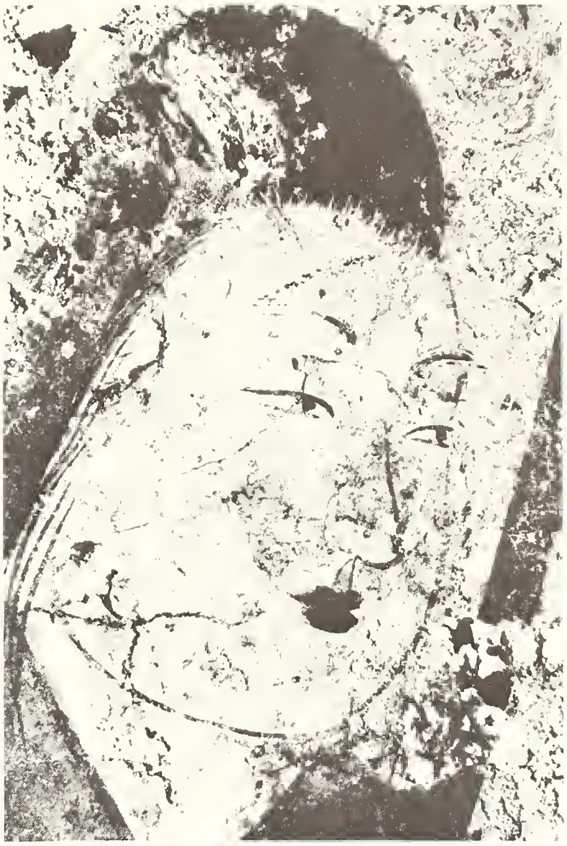

FIG. 4.—The face of the second woman from the right in the northern panel of the Western wall. × 1.3.

constellation on the ceiling.[9] The dimensions of the stone chamber and the positions of the figures are shown in Figure 2.

The northern panel of the western wall is in the best condition; it depicts four women in the pose of moving southward (fig. 3). The figures are rather small; the second woman from the right who stands looking backward is about 35 cm high. She wears a red jacket with a narrow blue band, and a long blue skirt with black stripes, and she holds a priest's staff resembling a mace. An enlargement of her face is shown in Figure 4. A celestial constellation is represented in the middle of the ceiling, each star being indicated by a round piece of gold foil, about 1 cm in diameter; the stars are connected with red lines (cinnabar). In this painting the brightness of the colors is admirable, and the technique is highly developed compared with primitive pigments used in the protohistoric tombs in Kyūshū. Although nothing has been found to indicate the name of the buried man, this tomb is judged by various pieces of evidence to have been made between the late seventh and early eighth centuries, after the introduction of advanced painting techniques which came with Buddhism in the sixth century. The pigments so far found in the

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[9] Kazuo Yamasaki and Yoshimichi Emoto, "Technical Studies on the Painting of the Newly found Tomb Takamatsuzuka in Central Japan", *Bulletin de l'Institut royal du Patrimoine Artistique*, vol. 15 (1975), p. 420.

Table 2
Pigments Used in the Takamatsuzuka Tomb and Hōryūji Paintings (7th–8th centuries)

Color	Takamatsuzuka Tomb	Hōryūji Temple, Golden Hall
ground coating	lime plaster	clay
white	presence of lead white suspected	clay
red	cinnabar red ochre —	cinnabar red ochre red lead
yellow	yellow ochre —	yellow ochre litharge*
green	malachite	malachite
blue	azurite	azurite
black	Chinese ink	Chinese ink
pink	possibly a mixture of red and white	—
others	gold silver	—

*Litharge is found only in the main wall paintings, not in the 20 small paintings representing flying angels.

painting of Takamatsuzuka tomb are listed in Table 2 (see footnote 9). The purity of lime plaster used as the ground coating was found to be 89.0–96.3% $CaCO_3$. Since a fragment of lime plaster contained Pb (1630 ppm), the use of lead white as a pigment is suspected. Gold foil was found by the atomic absorption method to contain Cu (0.02%) and Ag (2.2%).

WALL PAINTINGS IN BUDDHIST TEMPLES

Buddhism, which was introduced in Japan in the middle of the sixth century, spread gradually into the country; many Buddhist temples were built and Buddhist paintings made. The introduction of Buddhism brought with it a new technique and new coloring materials on which Japanese painting has been based ever since. According to documentary evidence,[10] in the 18th year of Empress Suiko (610 A.D.) a monk named Donchō from the Koguryō Kingdom on the Korean peninsula introduced to Japan the technique of preparing pigments and painting materials, and in the sixth year of Empress Jitō (692 A.D.) another monk, Kanjō, was rewarded by the Empress for preparing lead white for the first time in Japan.

About seventy wall paintings and architectural interior decorations made in various periods are now extent in Japan, mostly in Buddhist temples. All of them are painted on wooden panels or doors with three exceptions: a mud wall painting in the Hōryūji temple, and two wall paintings on lime plaster in the Hōkaiji temple (Kyōto) and the Hokuendo, Kōfukuji temple (Nara), respectively. About forty of these wall paintings and architectural interior decorations, including all the important ones, have been studied by Yamasaki in about thirty years since 1940. The results are listed in Table 3. Several more wall paintings were examined, but they had undergone later repairs and so were not included in the table. Numerous screen and sliding door paintings of the Momoyama and early Edo periods were also studied.

Hōryūji Temple

The Hōryūji near Nara is one of the oldest temples which survives to the present day, and it preserves many examples of early Buddhist art. The inner walls of the sanctuary

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[10] *Nihon Shoki* or *Nihongi*. English translation: W. G. Aston (translator), *Nihongi, Chronicles of Japan from the Earliest Times to A.D. 697* (The Japan Society, London, 1896; Kegan Paul, Trench, Trubner, 1924; Charles E. Tuttle Co., 1972).

TABLE 3

White Pigments on Wall Paintings and Architectural Interior Decorations (*indicates the latter)

	Name of Temple, etc.	Pigment
	Nara period (645–793)	
1.	Hōryūji, Golden Hall, Nara pref.	clay
2.	Hōryūji, pagoda,[†] Nara pref.	clay
3.*	Yakushiji, pagoda, Nara city	clay
4.*	Eizanji, octagonal hall, Nara pref.	clay
5.	Tōshōdaiji, Golden Hall, Nara city	clay
	Heian period (794–1185)	
6.	Taimaji, pagoda, Nara pref.	clay
7.	Murōji, Golden Hall, Nara pref.	clay
8.	Jōruriji, pagoda, Nara pref.	clay
9.	Daigoji, pagoda, Kyōto city	clay
10.	Hō-ōdō, Byōdōin, Kyōto pref.	clay
11.	Ujikami shrine, Kyōto pref.	clay
12.	Sanzenin, Amitabha hall, Kyōto city	clay
13.*	Hokaiji, Amitabha hall,[‡] Kyōto city	clay
14.	Kakurinji, Taishidō hall, Hyōgo pref.	clay
15.	Fukiji, main hall, Ōita pref.	clay
	Kamakura period (1186–1392)	
16.	Kaijūsenji, pagoda, Kyōto pref.	clay
17.	Hōshakuji, wooden tablet, Kyōto pref.	clay
18.	Daihō-onji (Senbon Shakadō), main hall, Kyōto city	clay
19.	Ryōzenji, pagoda, Nara city	clay
20.	Gansenji, pagoda, Nara pref.	clay
21.	Kōfukuji, pagoda, Nara city	clay
22.	Gangōji Gokurakuin, main hall, Nara city	clay
23.*	Kongōsanmaiin, pagoda, Wakayama pref.	clay
24.	Jōmyōji, pagoda, Wakayama pref.	clay
25.	Ishitedera, pagoda, Ehime pref.	clay
26.	Myō-ōin, pagoda, Hiroshima pref.	clay
27.	Ishiyamadera, pagoda, Shiga pref.	clay
28.	Shōmyōji, main hall, Yokohama city	clay
	Muromachi period (1393–1573)	
29.	Hōkanji, pagoda, Kyōto city	shell white
30.	Kanshinji, main hall, Ōsaka pref.	shell white
31.	Hōdōji, pagoda, Ōsaka pref.	clay
32.	Jōrakuji, pagoda, Shiga pref.	clay
33.*	Kōjōji, pagoda, Hiroshima pref.	clay
34.	Shin-hasedera, pagoda, Gifu pref.	clay
	Momoyama Period (1574–1614)	
35.	Kongōji, pagoda, Ōsaka pref.	shell white
36.	Nanzenji, sliding doors, Kyōto city	shell white
37.	Onjōji (Miidera), sliding doors, Ōtsu city	shell white
38.	Daikakuji, sliding doors, Kyōto city	shell white
39.	Myoshinji, sliding doors, Kyōto city	shell white
40.	Nijō castle, sliding doors, Kyōto city	shell white
	Edo Period (1615–1866)	
41.	Futaiji, pagoda, Nara city (early Edo period).	shell white
42.	Kyō-ōgokokuji (Tōji), pagoda, Kyōto city (early Edo period)	shell white

[†] Only traces of Buddhist figures were found under the surface layer applied later.

[‡] The wall paintings representing flying angels are painted on lime plaster walls, but Buddhist figures on pillars and other parts of architecture are painted with clay as the white pigment.

of the Golden Hall of the Hōryūji temple were decorated with brilliant paintings of the late seventh–early eighth century; they were severely damaged by a fire in 1949. These paintings consist of four large units (ca. 3 m × 2.5 m) and eight smaller ones (ca. 3 m × 1.5 m). Each of the large walls represented a Buddhist paradise and the small wall a figure of Bodhisattva. The walls were made of a mixture of mud and sand with straw bits as a binder. The surface of the walls was coated with fine white clay upon which the Buddhist figures were painted with the mineral pigments listed in Table 2.[11] As well as the main wall painting, near the ceiling of the inner sanctuary were twenty small panels on which were painted flying Buddhist figures. These small panels escaped the fire, and are now kept in a storehouse. Each one is about 75 cm × 140 cm and 15 cm thick, and was made in a similar way to the main wall painting. The pigments used were nearly the same (Table 2).

The painting technique for both the Takamatsuzuka and Hōryūji paintings is most accomplished. They are presumed to have been made between the late seventh and early eighth centuries, but pigment studies have so far given no information on which to base more exact dates.

Wall Paintings of the Later Periods

In addition to the wall painting of the Hōryūji temple, pigments of about forty wall paintings of the later periods, especially those of the Daigoji pagoda[12] and the Phoenix Hall (Hō-ōdō)[13] have been studied.

In the five-storied pagoda of the Daigoji temple, Kyōto, which has remained largely intact since the time of its original construction in 951 A.D., are found paintings showing the eight patriarchs of Shingon Buddhism and the mandalas of Vajradhatu and Garbhadhatu. The interior of the pagoda is covered with decorative patterns. The Phoenix Hall (Hō-ōdō) of the Byōdōin temple, at Uji, near Kyōto, was built in 1053 A.D. by the Fujiwara family which had an influential political power in the imperial court at that time. The inside walls and the doors of the Phoenix Hall are covered with scenes of Amitabha and his attendants coming down to earth to accompany the souls of the dead to the paradise of the Buddha. The pillars and other architectual parts are also covered with ornamental patterns. The pigments found in these two paintings are listed in Table 4 together with those found on sliding doors in various temples of later periods.

TABLE 4

Pigments Used in the Wall Paintings of the Daigoji Pagoda (10th Century), Hō-ōdō, (Phoenix Hall) (11th century), and in the Sliding Doors (16th–17th Centuries)

Color	Daigoji	Phoenix Hall	Sliding Doors*
white	clay	clay	shell white
red	cinnabar	cinnabar	cinnabar
	red ochre	red ochre	red ochre
	red lead	red lead	red lead
yellow	litharge	litharge	—
	yellow ochre(?)	yellow ochre	yellow ochre
green	malachite	malachite	malachite
blue	—	azurite	azurite
	substitute for azurite	substitute for azurite	—
black	Chinese ink	Chinese ink	Chinese ink
others	gold	gold	gold, silver

* Summary of the results on the sliding doors of Nanzenji and other temples, and those of the Nijō castle (Nos. 36–40, Table 3).

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[11] Kazuo Yamasaki, "Recent Technical Studies of Works of Art in Japan", *Application of Science in Examination of Works of Art, Proceedings of the Seminar, 1970* (Boston: Museum of Fine Arts, 1973), pp. 229–234 and Figure 7.

[12] Kazuo Yamasaki, "*Saishiki Ganryō* (Coloring Materials)", *Daigoji Gojūnotō Hekiga* (Wall Paintings in Daigoji Pagoda), edited by Osamu Takata (Tokyo: Yoshikawa Kōbunkan. 1959), pp. 187–194.

[13] Kazuo Yamasaki, "*Hō-ōdō no Saishiki ni mochi-irareta Ganryō ni tsuite* (On the Pigments used for coloring the Phoenix Hall)", *Bukkyō Geijutsu* (Ars Buddhica), no. 31(1957), pp. 62–64.

Changes in the kinds of pigments used throughout the long periods from the seventh to the seventeenth centuries are remarkable in some points. The most significant change is in the use of powdered oyster shell (calcium carbonate) as the white pigment instead of clay which had been used since the seventh century (see Table 3). This change or replacement seems to have taken place at some time in the fifteenth–sixteenth centuries. Accurate determination of the date of change is difficult, as there are very few examples from that period of precisely dated wall paintings that have not been later retouched. The birth of the Kanō school of painting might be related to the introduction of this new pigment, shell white.

Another change was the use of a substitute for azurite in the ninth through eleventh centuries. This substitute for azurite, made by dyeing yellow ochre with indigo, was first found in the wall painting of the Phoenix Hall (1053 A.D.).[13] The original blue color was almost completely lost due to exposure in the air for about 900 years, but from the margin of the painting concealed under a frame a bluish color appeared during the repair work, and indigo was chemically identified. The same substitute for azurite has been found in the painting of the Daigoji pagoda (951 A.D.), and also on the wooden halos of several statues (late ninth century) in the Murōji temple, Nara prefecture, and on a statue (eleventh century) of the Ryōzenji temple, Nara.[14] This substitute is not mentioned in the documents concerning pigments, and the reason for its use is not known. Perhaps the production of azurite or its importation from abroad was difficult in the late ninth through eleventh centuries. After the twelfth–thirteenth centuries azurite was again used in wall paintings.

In the sixteenth century, when warriors like Nobunaga Oda and Hideyoshi Toyotomi gained political power over the whole country, a grandiose style of painting was born. Many pictures were painted on sliding doors and folding screens of newly built castles and palaces. The themes were landscapes, birds and flowers, rather than Buddhist motifs. In these paintings on paper, gold was profusely used in leaf and powder forms, and pigments were applied in thick layers. The palette of the painters of these screen and door paintings, including the extensive Kanō school, was nearly the same as those of modern Japanese painters. The pigments found in some of these screen and door paintings are given in Tables 3 and 4.

OTHER KINDS OF PAINTINGS

Paintings in the Shōsōin Treasure House

The Shōsōin Repository or treasure house was originally a storehouse belonging to the Tōdaiji temple, the temple of Great Buddha in Nara; it is situated near the Hall of the Great Buddha. The Shōsōin Repository has kept its treasures under very strict custody, under an imperial seal. They are roughly divided into two groups. One consists of the objects offered to the Great Buddha by the Empress Dowager Kōmyō in 756 A.D. after the death of the Emperor Shōmu, who had built the Great Buddha in 752 A.D. The other comprises various objects used at the completion ceremony of the Great Buddha in

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[14] Kazuo Yamasaki, "*Kondō Itae oyobi Kondō Shobutsu no Itakohai no Saishiki no Ganryō* (Coloration of the Wall Painting of the Golden Hall, and of the Wooden Halos of Buddhist Figures in the Golden Hall)", *Yamato Koji Taikan* (General Survey of the Old Temples in the Yamato Province), vol. 6 *Murōji*, pp. 49–52 (Tokyo: Iwanami Shoten, 1976).

TABLE 5

Pigments Used in the Paintings and Handicrafts of the Shōsōin Repository (mostly 8th Century)

Color	Pigments
white	clay lead white
red	cinnabar red ochre red lead Sappan wood lake unidentified organic dye
yellow	yellow ochre gamboge
green	malachite
blue	azurite indigo
violet	unidentified, possibly organic
black	Chinese ink
others	gold, silver

752 A.D. In addition to these objects there are some other treasures introduced later into the Repository, in the eleventh century, for example. Among the various treasures are paintings, sculpture, metalwork, woodwork, lacquer wares, glass wares, ceramics and textiles.[15]

There are also in the Shōsōin various kinds of handicrafts and paintings of the eighth century in which oil was used as the medium for pigments applied on wood, Japanese lacquer or leather. There are two kinds of technique in the use of oil: one is the oil painting technique in which pigments mixed with oil are used, and the other is the application of oil over a painting in which animal glue was used as the medium, that is, glue tempera. The evidence for the use of oil is the occurrence of a yellow fluorescence under ultraviolet light. These oil paintings in the Shōsōin are the oldest ones remaining in Japan. The history of oil paintings in the Far East seems to be traceable back to the pre-Han period in China by documentary evidence, but no relics of that period have so far been found.[15]

In addition to these oil paintings various Buddhistic and non-Buddhistic paintings made on silk, hemp and paper have been preserved in the Shōsōin. The pigments used in various kinds of paintings and handicrafts are listed in Table 5.

Besides the pigments actually used on paintings, several samples of unused pigments of the eighth century were kept in the Shōsōin.[16] These are red lead, silver powder and lead white. The red lead is in powder form and amounts to more than 100 kg. It is contained in 128 small paper packages and consists of fine orange colored particles with a diameter of 0.005–0.01 mm. There are three grades: superior, medium and low. The chemical compositions are given in Table 6. As is clearly shown, these red lead samples are very low in Pb_3O_4 content as compared with a modern sample. A lump of white

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[15] Kazuo Yamasaki, "Technical Studies on the Ancient Art Objects in Japan, with Special Reference to the Treasures Preserved in the Shōsōin", *Application of Science in Examination of Works of Art, Proceedings of the Seminar, 1965* (Boston: Museum of Fine Arts, 1967), pp. 114–125 and fig. 18; *idem.*, "*Shōsōin Kaiga no Gihō to Zaishitsu* (Techniques and Materials of the Shōsōin Paintings)", *Shōsōin no Kaiga* (*Shōsōin Paintings*). (Tokyo: Nihon Keizai Shinbun Sha, 1968) pp. 155–162.

[16] During 1948–1951 an extensive scientific examination of the medicines preserved in the Shosōin was carried out, and the results were published. Yasuhiko Asahina (Editor), *Shōsōin Yakubutsu* (Shōsōin Medicinals) (Ōsaka: Shokubutsu Bunken Kankōkai, 1955). In this book Yamasaki has published the results of chemical analyses of red lead and silver powder. See also K. Yamasaki, "Chemical Studies on the Eighth-Century Red Lead preserved in the Shōsōin at Nara", *Studies in Conservation*, vol. 4 (1959), p. 1.

Table 6

Chemical Compositions of Red Lead Preserved in the Shōsōin
(8th Century)

	Superior	Medium	Low	Modern Red Lead
H_2O	0.06	0.06	0.08	—
acid insoluble	0.35	0.42	0.24	0.48
Pb metal	0.82	0.63	0.58	—
Pb_3O_4	26.20	23.98	6.17	78.10
PbO	70.90	73.00	92.20	21.10
Ag metal	trace	trace	trace	—
Fe_2O_3	0.01	0.02	0.02	—
Al_2O_3	0.23	0.54	0.37	—
CuO	0.03	0.01	0.04	—
CaO	0.18	0.12	0.12	—
MgO	0.03	0.04	0.01	—
total	98.81%	98.82%	99.83%	99.68%

substance in stick form is preserved which is supposed to be lead white from its apparent density (ca. 4), but no chemical examination has yet been made. The silver powder consists of particles with a diameter of 0.05–0.5 mm with the following chemical composition: Ag 94.17%, Au 1.14%, Cu 0.84%, a substance insoluble in aqua regia 0.57%, total 96.72%. There were also undetermined minor components and oxygen in the sample.

Handscroll Painting (*Emakimono*)

In addition to wall, door, and screen paintings, the handscroll is another important form of painting in Japan. One of the early examples is the *E-Ingakyō* ("Illustrated Sutra of Causes and Effects") of the middle eighth century.[17] Another example is the famous *Genji Monogatari Emaki* (Scroll of the "Tale of Genji") of the first half of the twelfth century.[18] When these two scrolls were examined by X-radiography, ultraviolet illumination and infrared photography, some pigments not used in other kinds of paintings were found. They were gamboge, and unidentified organic coloring materials which are presumed to be of plant origin. The results are listed in Table 7.

An art historical study on the *Senmen Hokekyō Sasshi* (Fan-shaped Album of the "Lotus Sutra" with under-painting) of the mid-twelfth century carried out by T. Akiyama and T. Yanagisawa is also to be mentioned.[19] They used X-radiography and optical microscopy as the main tools to

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[17] Ichimatsu Tanaka (Editor). *Kōgakuteki Hōhō ni yoru Kobijutsuhin no Kenkyū* (Studies on Old Art Objects through Optical Methods) (Tokyo: Yoshikawa Kōbunkan, 1955) In this book two scrolls, *E-Ingakyō* and *Genji Monogatari Emaki* are described as examples of the scroll paintings. X-radiograms are given. 29 pages of English abstracts appended.

[18] Kazuo Yamasaki and Hidetarō Nakayama, "*Genji Monogatari Emaki no Ganryō ni tsuite* (On the Pigments used in the Scroll Painting of the Tale of Genji)". *Bijutsu Kenkyū*, no. 174 (March 1954), pp. 229–234. See also footnote 17.

[19] Terukazu Akiyama and Taka Yanagisawa, *Senmen Hokekyō* (Fan-shaped Album of the Lotus Sutra with under-painting) (Tokyo: Kashima Shuppan Kai, 1972).

TABLE 7

Pigments Used on Early Scroll Paintings

Color	E-Ingakyō	Tale of Genji
	(early 8th century)	(first half of the 12th century)
white	lead white	lead white
red	cinnabar	cinnabar
	red lead	red lead
	—	unidentified organic dye
yellow	gamboge	gamboge
green	malachite	malachite
blue	azurite	azurite
violet	—	unidentified organic dye
black	Chinese ink	Chinese ink
others	—	gold, silver

elucidate the technique of this painting. In small, precious paintings like scroll paintings, more expensive pigments like lead white and organic coloring materials are used, and no substitute for azurite has ever been found. More studies on scroll paintings are desirable.

Paintings in the 17th Century

The Momoyama period (1574–1614), in which many gorgeous screen and door paintings were made to decorate palaces, castles and temples was followed by the Edo period (1615–1866). In this period various schools of painting made their appearance, and rivalled each other in artistic works, mainly *kakemono* (hanging scrolls) and *byōbu* (folding screens), but these have not yet been studied by scientific methods in Japan. Therefore, a detailed study on pigments used in *Ukiyo-e* paintings, which belong to one of the Edo painting schools, carried out by R. J. Gettens and E. W. FitzHugh gives valuable information in this field.[20]

Recently E. Taguchi and M. Taguchi studied a scroll of the early Edo period, *Genji Monogatari 54-jō Emaki* (scroll representing 54 scenes of the "Tale of Genji"), made by a painter of the Kanō school; it has a possible date of 1695. Using a specially constructed spectrophotometer,[21] they succeeded in identifying the presence of laccaic acid (or carminic acid) in the reddish-purple part of the scroll. The identified coloring materials included vermilion, gamboge, malachite, azurite, indigo, a mixture of indigo and gamboge, a mixture of red lead, gamboge and Chinese ink, a mixture of vermilion and Chinese ink, and shell white, in addition to the above mentioned organic red color. For the painting technique of the Edo period there are several books such as *Honchō Gashi* ("History of Japanese Paintings") and *Honchō Gahō Taiden* ("Survey of Japanese Painting Techniques"). The former was edited by Einō Kanō and published in 1691, and the latter by Mitsuoki Tosa in 1690 which describes the technique of the Tosa school. Comparison of the pigments actually found in the paintings of the Edo period with those mentioned in these books describing painting techniques of that period will give useful information. The Taguchis have contributed to this field, and more studies along this line are to be pursued in the future.

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[20] R. J. Gettens, "Japanese Paintings—Technical Studies and Conservation at the Freer Gallery of Art", *Conservation and Restoration of Pictorial Art*, N. Brommelle and P. Smith, eds. (London: Butterworths, 1976), pp. 241–252. (Papers presented at the Lisbon Congress, IIC, 1972). E. W. FitzHugh, "A Pigment Census of Japanese Ukiyo-e Paintings in the Freer Gallery of Art," elsewhere in this volume.

[21] Ei-ichi Taguchi and Mamiko Taguchi, "*Bunkōgakuteki Hōhō ni yoru Ganryō, tokuni Yūki Shikiryō oyobi sono Chōgō Shoku no Hantei ni tsuite. Kinsei Shoki Kanōha Funpon, Genji Monogatari 54-jō Emaki, o rei to shite* (Spectrophotometric identification of coloring materials, especially of organic pigments and combined mixed colors—with reference to the pigments used in the scroll, *Genji Monogatari 54-jō Emaki*, of the Edo period)". *Kobunkazai no Kagaku* (Scientific Papers on Japanese Antiques and Art Crafts), no. 20/21 (August 1977), pp. 18–37. In this article a specially constructed spectrophotometer, Shimadzu MPS-5000, was used, and is now commercially available.

CHARACTERISTICS OF PIGMENTS USED IN JAPANESE PAINTINGS

In order to summarize the results of pigment studies on Japanese paintings several points are to be mentioned.

Ground coating. In the tombs of the Koguryō period in Korea and those of the Han period found in the northeastern part of China,[22] lime plaster was used as the ground coating, but no such case has been found in the protohistoric decorated tombs in Kyūshū (5th–6th centuries), in which pigments were applied directly on stone surfaces. The early seventh century Torazuka tomb in the eastern part of Japan, where a mixture of kaolinite, α-quartz and feldspar was used as the ground coating, is an exceptional case (fig. 1). In the wall paintings of the historical periods, those made on mud or lime plaster are few in number, and most of the wall paintings are painted on wooden panels or doors.

White pigments. In Japanese paintings of earlier periods clay was always used. This is one of the characteristic pigments of Japan, and was replaced by oyster shell white in the fifteenth–sixteenth centuries. Shell white has been continuously used throughout the Momoyama and Edo periods until today. Japan seems to be the only country where powdered oyster shell has been used as a white pigment. Lead white has also been used from the seventh century through seventeenth century, mostly in small and valuable paintings.

Red pigments. Cinnabar, red ochre, and red lead are the main red pigments used from the early historical periods. Natural cinnabar is found from the earliest times, but in later periods artificially made vermilion came into use. In 1609 monopoly guilds were founded in Edo (an earlier name for Tokyo) and Sakai, a port for foreign trade near Ōsaka, for the purpose of manufacture and trade of vermilion.

Yellow pigments. Litharge, yellow ochre, and gamboge were used through the ages, but litharge ceased to be used in later periods, probably because it is unstable in air, and its color is not bright.

Green pigments. Malachite is the only green pigment used not only in Japan, but also in Far Eastern paintings in general. Although *Nara Rokushō* (basic copper acetate) is mentioned in documents, it has not yet been found. In the protohistoric tombs in Kyūshū a powdered green-colored rock was used, in which glauconite has been identified by Emoto.[23]

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[22] Kazuo Yamasaki, "*Keiryō Hekiga no Ganryō* (Pigments used in the Wall Paintings of Ching-Ling)." *Bijutsu Kenkyū*, no. 153 (March 1949), pp. 99–100.

[23] Emoto, "Conservation of the Ōtsuka Tomb."

Blue pigments. Azurite is the main pigment used, but due to its scarcity and high price a substitute made by dyeing yellow ochre with indigo was used for a limited period, from the late ninth to eleventh centuries. Indigo was also used in various kinds of painting. Lapis lazuli (natural ultramarine blue) has never been found in paintings in Japan because it is not produced in Japan. In modern Japanese paintings a vitreous blue pigment is used as a substitute for azurite, which is now very expensive.

Violet pigments. Violet colors found in Japanese paintings are usually a mixture of red and blue pigments, such as cinnabar and azurite or cinnabar and indigo, but violet-colored pigments found in the handicrafts preserved in the Shōsōin, or in the scroll painting of the "Tale of Genji" (twelfth century) have not yet been identified. The use of organic dyes is suspected, and a more detailed study is desirable.

Black pigments, gold and silver. Chinese ink is the only black pigment used throughout the centuries except for carbon and a black manganese mineral found in protohistoric tombs in Kyūshū. Gold foil found in the Takamatsuzuka tomb (seventh–eighth centuries), and silver powder preserved in the Shōsōin (eighth century) are the examples analyzed chemically.

Organic dyes and lakes. Identification of organic dyes and lakes is much more difficult than mineral pigments. In some paintings red organic dyes were found, but they are not fully identified yet except for the recent example noted above. Spectrophotometric techniques developed recently have been useful in elucidating the nature of organic dyes, and will be used more in the future.

Vitreous pigments. It is not known when vitreous pigments which are made of colored glassy substances first came into use in Japan, but judging from the history of glass in Japan their origin seems to be later than the Meiji restoration (1867).[24] Vitreous pigments of various colors are now in the market which have very complicated chemical compositions as revealed by spectrochemical analysis.[25]

When one of the authors (K.Y.) began to study the pigments used in Japanese paintings about 40 years ago, very little was known about their chemical nature. Most art historians presumed without any evidence, for example, the use of shell white throughout all periods. Now it is clear that the pigments used are not the same for various periods. Progress of modern analytical techniques such as spectrophotometry[26] and electron microscopy[27] will give us more information in the future on the nature of coloring materials.

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[24] Personal opinion of K. Yamasaki, and private communication of Shin-ichi Ishida, Director of the Ishida Hōkōdō Pigment Company, Kyōto.

[25] K. Yamasaki, unpublished results.

[26] Taguchi and Taguchi, "Spectrophotometric Identification."

[27] Hachirō Oguchi, "*Nihonga no Chakushoku Zairyō ni kansuru Kagakuteki Kenkyū* (Scientific Investigation on Coloring Materials in Japanese Painting)." *Tokyo Geijutsu Daigaku Bijutsugakubu Kiyō* (Bulletin of the Faculty of Fine Arts, Tokyo University of Arts), no. 5 (July 1969), pp. 27–82; *idem.*, "*Sumi no Kenkyū* (Studies on Chinese Ink Stick)," *Kobunkazai no Kagaku* (Scientific Papers on Japanese Antiques and Art Crafts), no. 20/21 (August, 1977), pp. 38–66; John Winter, "Preliminary Investigations on Chinese Ink in Far Eastern Paintings," *Archaeological Chemistry*, Curt W. Beck (Editor), Advances in Chemistry Series, no. 138 (Washington, D.C.: American Chemical Society, 1974), pp. 207–225.

THE SCROLL PAINTING

BY KENZŌ TOISHI*

INTRODUCTION

Among the many contributions of Rutherford J. Gettens to the scientific study of works of art were a number of important studies on the materials of paintings.[1] His later interests in this area were centered around a research project on Japanese *Ukiyo-e* paintings in collaboration with E. W. FitzHugh, on which a first report was delivered to the Lisbon Congress of the International Institute for Conservation held in 1972.[2] This report deals with the materials, especially the pigments, found in Japanese paintings, the specialized training needed for conservators, and also with the approach to painting conservation adopted by the Freer Gallery. The latter relies extensively on "panel" mounting for *kakemono,* for reasons connected with the particular conditions of climate and storage there.

Gettens' Lisbon paper did not, however, deal with the properties of scroll mounting for oriental paintings, and this is the subject addressed in the present contribution. Scroll mounting for paintings is limited to countries of the Far East and appears to have been introduced to Japan from China along with the glue-medium technique of painting.

Japanese paintings of the type being considered here are normally on silk or paper supports, materials that undergo dimensional changes with varying atmospheric humidity, and also that have only a limited tensile strength. For these reasons the panel mounting[3] noted above may be vulnerable if the humidity is not controlled; it is indeed possible for a painting to be torn by the stress induced when the humidity decreases sharply. In the case of a scroll mounting, however, where the painting is lined with tough, long-fibered paper but remains flexible, such stresses are absorbed by small deformations. This feature is one of the main characteristics of scroll mounting. A second characteristic is that, when rolled, the scroll becomes very compact for storage. For Japanese paintings in Japan, the "stored state" is the normal state: a painting is exhibited only for brief periods when necessary. This convention appears to have done much for conservation.

The last point is especially significant since, as will be explained more fully below, the structure of a Japanese paint layer is a very porous one, with the pigment grains imperfectly covered and interpenetrated by glue medium. The presence of many minute air spaces in the layer may be seen by putting a drop of water on the painting and observing

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[*] Maruyama-2, Funabashi City, Japan.

[1] e.g.: Rutherford J. Gettens and George L. Stout, *Painting Materials, A Short Encyclopedia* (Van Nostrand Company, 1942; Dover Publications Inc., 1966). R. J. Gettens, E. W. FitzHugh, R. L. Feller, "Calcium carbonate whites," *Studies in Conservation*, Vol. 19 (1974), pp. 157–184, and previous articles in this series, cited therein.

[2] Rutherford J. Gettens, "Japanese paintings: technical studies at the Freer Gallery of Art," In *Conservation and Restoration of Pictorial Art*, edited by Norman Brommelle and Perry Smith, (Butterworths: London, 1976), pp. 241–252. Reprint of the Proceedings of the Lisbon Congress of the International Institute for Conservation, October 1972.

[3] H. Yamamoto and N. Usami, *Hyōgu no shiori* (Unsōdō, Kyoto, 1974). T. Okamura, *Gakuso no hanashi* (Okamura-tamondō: Tokyo, 1955).

the change in light-scattering by the pigment grains as the air spaces fill up. This feature of porosity in the paint layer makes it very susceptible to deterioration, and necessitates its protection in some way during storage. Since a scroll is stored rolled up, such protection is achieved automatically by the paint layer being held close to the back of another part of the painting.

As against this advantageous feature, certain drawbacks in scroll mounting will become evident during the discussion below.

SIMPLIFIED MODEL OF THE PAINT LAYER

In order to appreciate better the properties of the paint layer in a Japanese painting, let us first consider a simplified model. Though it is an imaginary, non-realizable case, we may, with caution, apply it to real paintings with appropriate modifications.

We assume the following: the paint layer consists of uniform, close-packed spherical grains of radius R, initially just completely interpenetrated with a 2% aqueous glue solution, painted on a surface that does not absorb glue. The force of gravity is neglected and desiccation occurs uniformly at all points. Edge effects at the two surfaces of the layer are also neglected.

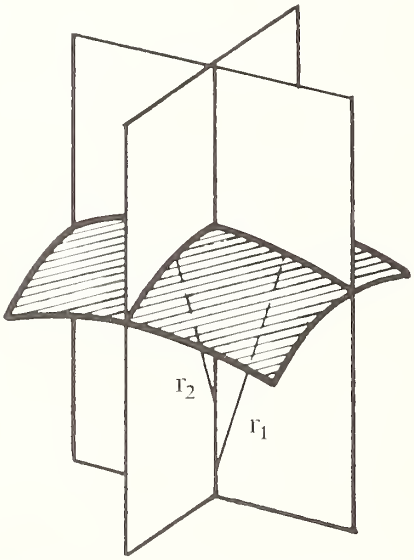

FIG. 1. The principal radii of curvature, r_1, r_2, of a liquid surface (shaded).

The packing fraction p (the proportion of the total volume occupied by the spheres themselves) for close-packed uniform spheres is $\pi/(3\sqrt{2}) = 0.74$ approx.[4] Initially, therefore, some 26% of the total volume is occupied by glue solution. As water evaporates, air spaces will appear in the interstices of the array of pigment grains. Let r_1, r_2 be the two principal radii of curvature of the liquid-air surface at any point (fig. 1). The pressure difference across the surface due to surface tension γ is given by $\gamma(1/r_1 + 1/r_2)$, the radius being taken as positive or negative according to whether the center of curvature is on the liquid or air side. It follows that, for a stable state, the algebraic sum of the curvatures $(1/r_1 + 1/r_2)$ must be constant over the whole surface.

Animal glue solutions are known to have an acute angle of contact with a pigment grain, and one that is probably quite small if not zero.[5] Accordingly, as the glue solution evaporates, we envisage a lens of liquid suspended between each pair of spheres in contact, as in Figure 2A. It is obvious by inspection that the situation in Figure 2B, with a layer of liquid spread over the whole of the grain, is ruled out by the "curvature condition" noted above. It is not possible for the algebraic sum of the principal curvatures at a point such as *a* to be the same as that at point *b*. It should also be noted that, in the present case, the pressure inside the liquid lens is decreased by the surface tension, resulting in an attractive force between the grains, which tends to maintain the condition of close packing.

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[4] H. S. M. Coxeter, *Introduction to Geometry* (John Wiley and Sons, 2nd edition, 1969), pp. 405–411. See also many texts dealing with crystal chemistry, including: A. F. Wells, *Structural Inorganic Chemistry* (Oxford: Clarendon Press, 4th edition 1975), chapter 4.

[5] The angle of contact between pure water and clean glass surface is 0°, but if water is not pure it takes a value amounting to several degrees. It is supposed that glue solution used in painting shows comparable angles of contact with mineral pigments in general. See: *International Critical Tables* (McGraw-Hill, for the National Research Council), Vol. 4, p. 434; *Rikagaku jiten* (Iwanami-shoten, Tokyo, 3rd edition, 1971) p. 727.

To calculate the volume of the liquid lens, we assume further that the air-surface of the lens is a cylinder. Let the semi-angle subtended at the center of the sphere be α (fig. 3). It can then be shown[6] that the required volume is given by:

$$v = \frac{2}{3}\pi R^3(1 - 3\operatorname{Cos}^2\alpha + 2\operatorname{Cos}^3\alpha)$$

The glue solution, which initially occupies the interstitial volume of the spheres, will have contracted to the sum of volumes of the liquid lenses represented above. Let the ratio of the initial to final volumes be q, then, with a packing fraction p it can further be shown[7] that:

$$[(1/p) - 1] = 3q(1 - 3\operatorname{Cos}^2\alpha + 2\operatorname{Cos}^3\alpha)$$

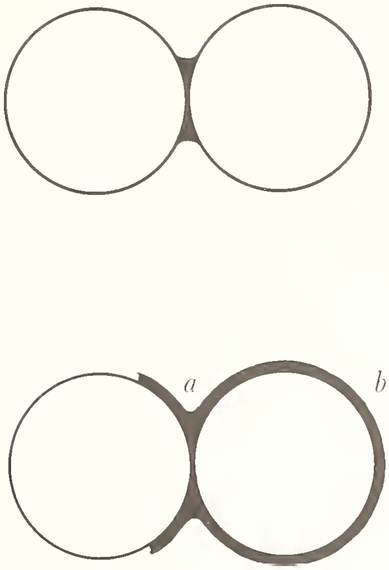

FIG. 2.—A (upper): lenticular drop of glue solution collected at the point of contact of two spherical pigment particles; B (lower): coverage of the entire particle surface by glue solution is not possible because of surface tension.

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[6] Vol. required, v = (Total volume of cylinder enclosed by liquid—air surface) − 2(Volume of spherical segment subtending semi-angle α). Hence:

$$v = 2\pi R^3\operatorname{Sin}^2\alpha(1 - \operatorname{Cos}\alpha) - \frac{2}{3}\pi h^2(3R - h)$$

where h = height of spherical segment = $R(1 - \operatorname{Cos}\alpha)$

$$\begin{aligned} v &= 2\pi R^3\operatorname{Sin}^2\alpha(1 - \operatorname{Cos}\alpha) - \frac{2}{3}\pi R^3[3(1 - \operatorname{Cos}\alpha)^2 \\ &\qquad - (1 - \operatorname{Cos}\alpha)^3] \\ &= 2\pi R^3[(1 - \operatorname{Cos}^2\alpha)(1 - \operatorname{Cos}\alpha) - (1 - \operatorname{Cos}\alpha)^2 \\ &\qquad + \frac{1}{3}(1 - \operatorname{Cos}\alpha)^3] \\ &= \frac{2}{3}\pi R^3(1 - 3\operatorname{Cos}^2\alpha + 2\operatorname{Cos}^3\alpha). \end{aligned}$$

[7] In close-packing, each sphere touches 12 others, thus 12 lenses of liquid are involved, each shared with one other sphere. Hence the volume of liquid associated with one sphere is 6v. If the volume of a polyhedron around one sphere is V,

then $\dfrac{(4/3)\pi R^3}{V} = p$ (the packing fraction)

or $V = (4/3)\pi R^3(1/p)$

Volume of void associated with one sphere in close-packing = $V - (4/3)\pi R^3 = (4/3)\pi R^3(1/p - 1)$.

This is the initial volume of glue solution associated with one sphere, which contracts to volume 6v. This contraction is the ratio q.

Hence $\dfrac{(4/3)\pi R^3(1/p - 1)}{4\pi R^3(1 - 3\operatorname{Cos}^2\alpha + 2\operatorname{Cos}^3\alpha)} = q$

or $(1/p - 1) = 3q(1 - 3\operatorname{Cos}^2\alpha + 2\operatorname{Cos}^3\alpha)$

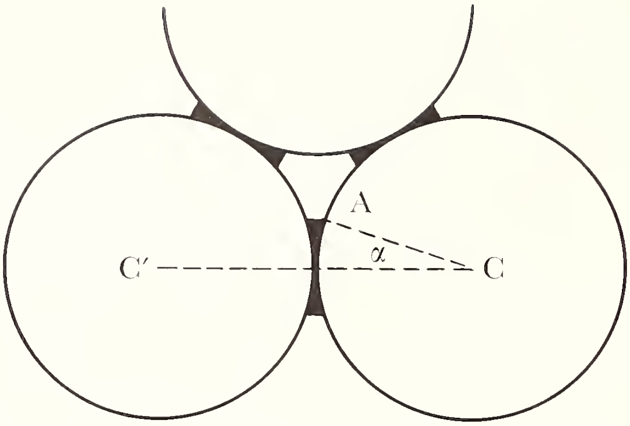

FIG. 3.—Three touching pigment particles with lenses of glue solution subtending semi-angle α at the center of a particle.

If we start with a 2% glue solution, and suppose that gelatinization occurs at a concentration of 10% (approximately true for cool conditions, e.g., in the wintertime), then $q = 5$. Since $p = \pi/(3\sqrt{2})$, we obtain:

$$30 \operatorname{Cos}^3 \alpha - 45 \operatorname{Cos}^2 \alpha + 16 - 3\sqrt{2}/\pi = 0$$

This equation is satisfied by $\alpha = 24°38'$ ($\operatorname{Cos} \alpha = 0.90894$).

One lens covers an area on the surface of the spherical grain of $2\pi R^2(1 - \operatorname{Cos} \alpha)$; as there are twelve such lenses the proportion of the surface covered becomes $6(1 - \operatorname{Cos} \alpha)$. For $\operatorname{Cos} \alpha = 0.90894$ this proportion is 0.55. Therefore, around 50% of the surface area of the pigment grains will be covered by glue gel.

Further dehydration of the glue after gelatinization will of course make its volume smaller, even though it is no longer behaving as a liquid. This may in some cases result in fracturing of the glue itself, or in failure of its adhesion to the pigment grain. If there is any effect on the exposed area of the grain, it will be to make that area greater.

We conclude from this model that a very porous paint layer is to be expected in a Japanese painting, with the interstices between pigment grains partly occupied by air, and of the order of 50% of their surface area covered by the glue medium.

CORRECTING CONSIDERATIONS FOR REAL CASES

The various assumptions made for the above treatment all, of course, contradict reality. Pigment grains are of irregular shape and non-uniform size, and are unlikely to be close-packed, so that their distribution in space is much less simple than that used here. The effect of gravity on the drying paint layer is likely to be partly offset by capillarity effects, but the result may be a departure from uniformity in the glue distribution. The calculation for the volumes of the lens-shaped drops at the contact points of spheres has been oversimplied by assuming a cylindrical shape for the air-surface. A more accurate treatment would predict a larger surface coverage of the pigment grains. On the other hand, absorption of glue by the support (in practice minimized by sizing of the support) would decrease the amount of glue present. Also, of course, the figures assumed for glue concentrations of 2% initially and 10% for gelling are only approximations. Even taking into account all of these points, however, the following conclusions appear to be justified for real paintings.

(a) The glue medium in the paint layer is less than that required for complete coverage and complete protection of the pigment particles.

(b) The glue medium present will tend to accumulate at the points of contact of the grains.

(c) As a consequence, a generally "lean" or porous paint layer is anticipated, and, indeed, observed in practice.

MERITS OF THE SCROLL

A pigment layer of the type described above easily deteriorates, and it is advisable to protect it in some way. However, to apply a transparent coating, such as a synthetic resin, would change completely the aesthetics of the painting and consequently has always been found unacceptable. Protection during storage is achieved for a scroll by the fact of the scroll being rolled up.

In fact, protection by rolling in this way is likely to be more efficient than, for example, any attempt to cover a plane surface with a protective sheet. Even in scrolls where the outer brocades are thicker than the painting itself and, as a consequence, contact of the face of the painting with the backing next to it is not uniform, it is expected that air and light will be excluded, and a good measure of protection thus achieved.

The second merit of a scroll mounting is that it becomes very compact when rolled for storage. Generally, a scroll will be stored in a plain, unvarnished box of paulownia wood (Japanese: *kiri*), itself placed in a lacquered wooden box (fig. 4). The lacquered box functions as a moisture barrier and the plain inner box acts as a humidity buffer[8] and is also a good shock absorber.

The third merit of scroll mounting is that the flexibility of the whole assembly avoids the possibility of large stresses acting on the painting. The lining attached to the support is itself a flexible sheet of paper. Since the mounting is not attached to a rigid structure, incidental forces do not have to be accepted by the support, but rather are allowed to deform the painting slightly. In Japan, many paintings are found mounted as rigid panels, for example on sliding doors, folding screens and other furniture. In such paintings deterioration of the pigment layer is generally far greater than in scrolls, and there have been examples of the support being torn as a result of humidity changes. Both types of deterioration tend to be avoided in a flexible scroll, which is usually kept rolled up in storage.

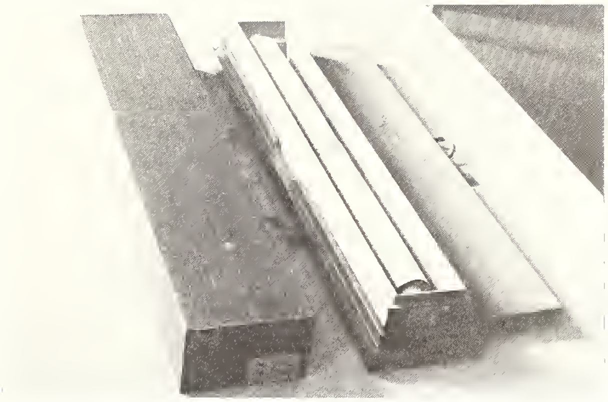

Fig. 4.—Inner and outer boxes for the storage of scrolls.

The fact that deformations of the support are possible leads, however, to certain weaknesses of scroll mounting, dealt with in the following section.

DEMERITS OF THE SCROLL

The normal state of the scroll is rolled up for storage. The problems that occur are usually in connection with its being unrolled for exhibition, and may be classified as mechanical deformations and as deterioration that occurs as a result.

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[8] K. Toishi and T. Kenjō, "Difference of wood materials as buffer against change of atmospheric humidity," *Science for Conservation*, No. 6 (1970), pp. 25–36.

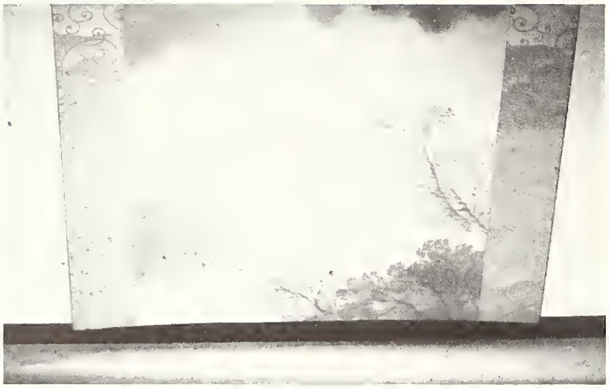

Fig. 5.—Unrolling a scroll to show a lateral concavity from the front.

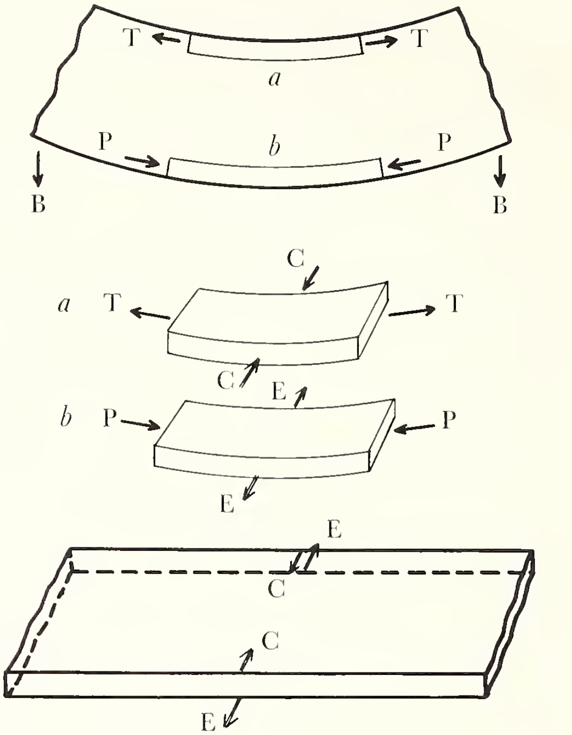

Fig. 6.—Forces acting on a scroll during unrolling: *a* is an "inside" surface layer subject to tension T and undergoing negative lateral strain C; *b* is an "outside" surface layer subject to compression P and undergoing positive lateral strain E.

Deformation

When a scroll, especially a hanging scroll, is unrolled, the painted surface often becomes concave (fig. 5). This arises as follows. When the painting is stored for a long time, the rolled shape becomes, as a result of creep, the natural shape of the scroll. When it is unrolled a layer along the painted surface (*a* in fig. 6) experiences a tension T to extend it longitudinally, and a layer along the back surface (*b* in fig. 6) experiences a compressive force P to make it contract. The fibrous, network-like structure of paper[9] leads to the converse dimensional displacements C and E occurring in a lateral direction, i.e., the front surface tends to contract and the back to expand, leading to a concavity (as seen from the front) in lateral section. We call this first-stage deformation, and it is reversible: if the scroll is again rolled, it reverts to the original shape.

However, if the scroll is allowed to hang for a sufficiently long period, it undergoes a second-stage deformation that is irreversible. Consider the scroll to be divided into five vertical zones (fig. 7). The lateral curvature from first-stage deformation causes zone 3 to be behind a median plane defined by the roller (at the bottom) and the top bar, and zones 1 and 5 to be in front of that plane. As a result, the weight of the roller tends to be concentrated on these three zones, with zones 2 and 4 relatively unstressed. The central zone, 3, is thus pushed forward, though against the resistance of zones 2 and 4. Zone 1 (and, *mutatis mutandis*, zone 5) is pulled back and, having a free edge, can move relatively easily, inducing a reversed curve in zone 2. The stresses themselves will tend to be displaced as a result of these movements, into the previously unstressed areas. In sum, the scroll gradually

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[9] S. Oguri, *Nihonshi no hanashi* (Waseda Univ. Press, Tokyo, 1953). B. Jugaku and others, *Shōsōin no kami* (Nihon-keizai shinbunsha: Tokyo, 1970).

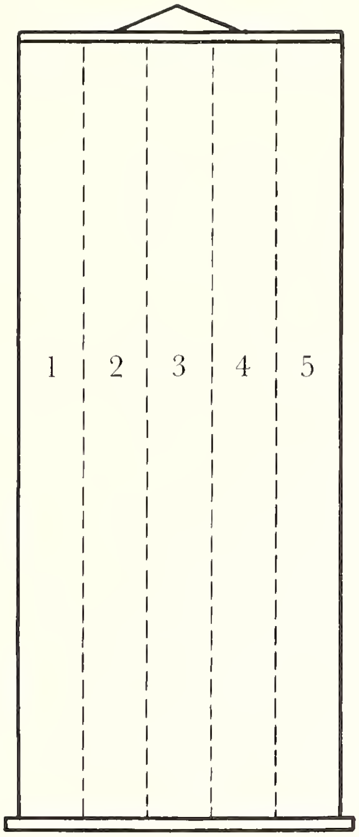

Fig. 7.—Five zones of a hanging scroll used to analyze the progress of second-stage deformation (see text).

deforms into a "wavy" shape, and, eventually, adopts the form shown in cross section in Figure 8. Figure 9 illustrates a scroll that has deformed in this way: the shadow thrown by a taut string indicates the shape of the surface.

As noted above, this second-stage deformation is irreversible. If such a deformed scroll is re-rolled, it will not roll up in an even fashion. Sometimes, though rarely, fine longitudinal creases can occur in zones 2, 3 and 4 as a result of stresses caused by re-rolling.

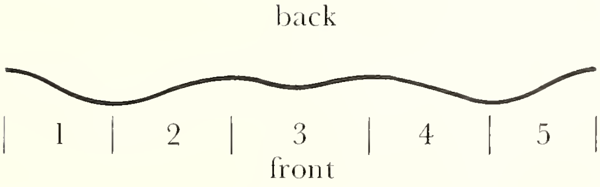

Fig. 8.—Lateral section through a scroll after second-stage deformation has occurred.

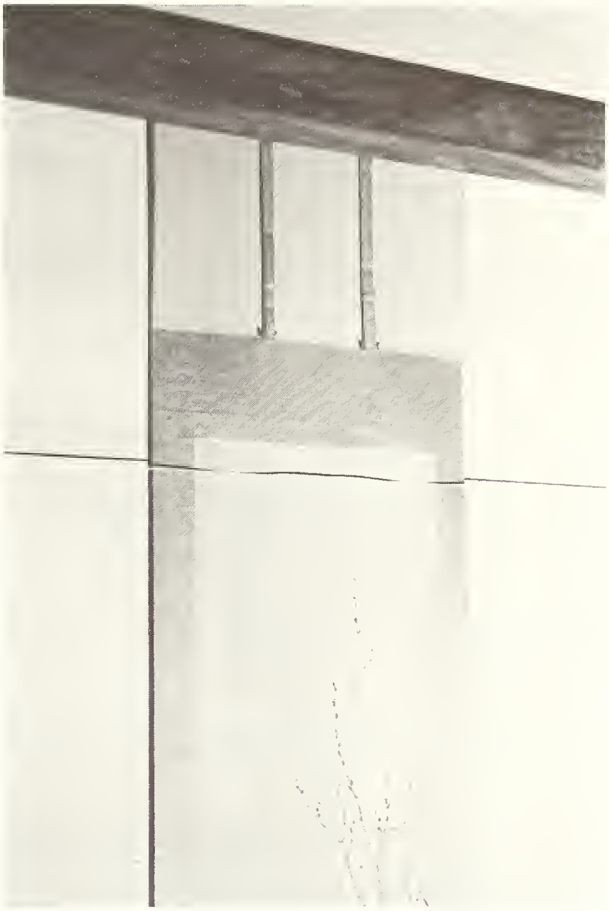

Fig. 9.—Shadow cast by a taut string shows second-stage deformation in a hanging scroll.

Second-stage deformation is observed to occur within a few years in ordinary climatic conditions; it is not observed in the exhibition period of one month usually insisted on in Japan.

Deterioration

The deformations above are important if the paper used for the scroll is relatively new

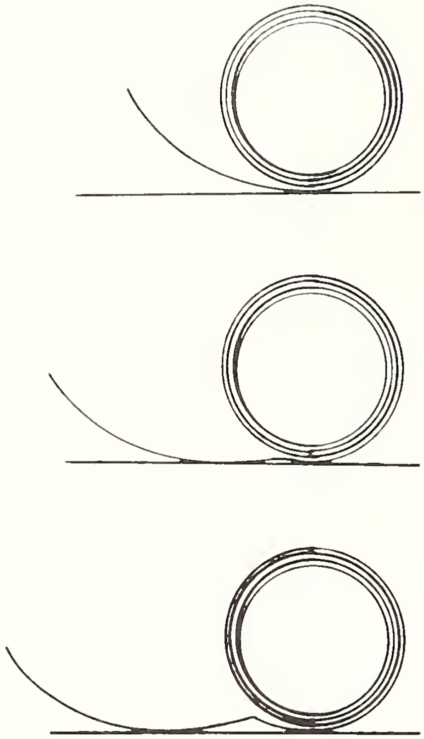

FIG. 10.—Lateral cracking may occur as a scroll unrolls.

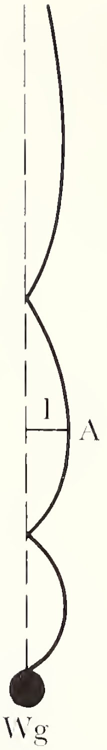

FIG. 11.—Stressing of a hanging scroll with lateral cracks.

and in good condition. Deterioration causes it to be brittle,[10] leading to the production of lateral cracks and creases caused from the bending forces that occur during unrolling (fig. 10). Such creases appear more often where the bending forces are larger, that is, near the roller where the curvature is greater. Figure 11 shows the bending moment arising from the weight of the roller acting on a displayed hanging scroll that has already developed rolling cracks. The bending moment at any point A is Wgl, where W is the total mass of the scroll and roller below A, l the perpendicular distance of A from the vertical line through the center of gravity of the mass, and g the acceleration due to gravity. Clearly this moment reaches maximum values where l is greatest, that is, where the curve of the paper is furthest from the central line. If the mounting is brittle enough, new cracks have the greatest chance of forming at these points.

The handscroll is usually far longer than the hanging scroll, the width being rather smaller. In order to make the rolled scroll compact, thinner paper is used. Accordingly, the mounting is rather flexible, reducing the magnitude of the bending forces; even so, lateral creases are often seen towards the roller end. In addition, longitudinal creases are often seen in handscrolls (fig. 12). These are thought to have come from careless treatment by previous owners. A handscroll is viewed by unrolling it from the right to bring successive parts into view, the right-hand end being rolled up again (fig. 13). The roll on the

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[10] S. Katō, *Washi* (Tōkyō-denki Univ. Press: Tokyo, 1966).

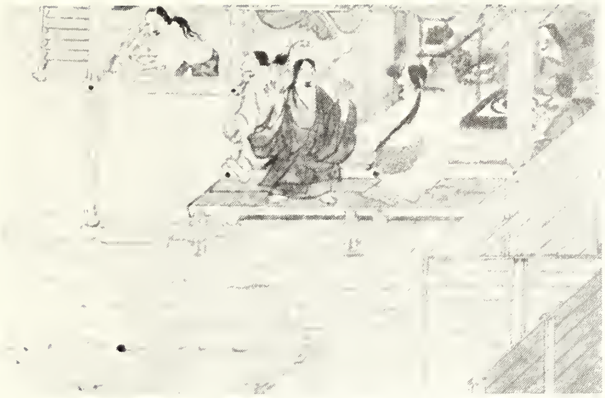

FIG. 12.—Longitudinal creases in a handscroll, arising from careless handling.

left, being supported by the roller, will withstand hand pressure comparatively well, but that on the right is hollow and therefore vulnerable. Pressure on this roll pushes the paper in as shown, making a longitudinal crease. Accordingly, such creases appear where the hands, especially the thumbs, are most often placed.

Figure 14 shows a vertical crease of a type arising occasionally from the pressure of the braid used for tying the rolled scroll, when it has been tied too tightly.

Where a thickly painted picture is mounted as a scroll, flaking of the paint layer occurs easily from the mechanical effect of rolling and unrolling. Accordingly, it is better that paintings to be scroll-mounted should have paint layers thin enough to be sufficiently flexible.

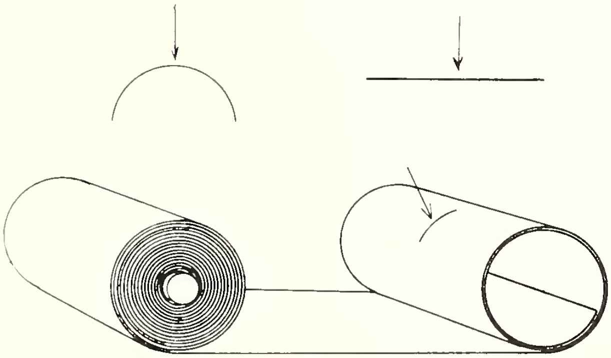

FIG. 13.—Unrolling a handscroll. The unsupported roll on the right is vulnerable to handling damage.

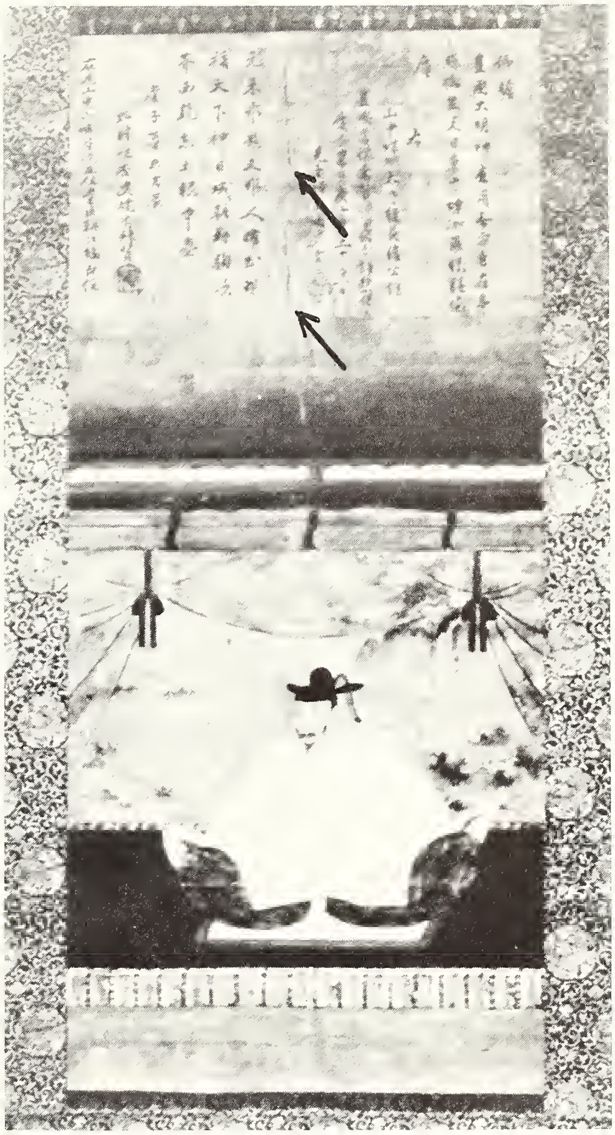

FIG. 14.—Damage from the pressure of a too-tightly tied braid (see arrows).

Lateral cracking of the scroll, as noted above, is connected intimately with the curvature on rolling, so that it is useful to make the roller thicker and therefore the curvature less.

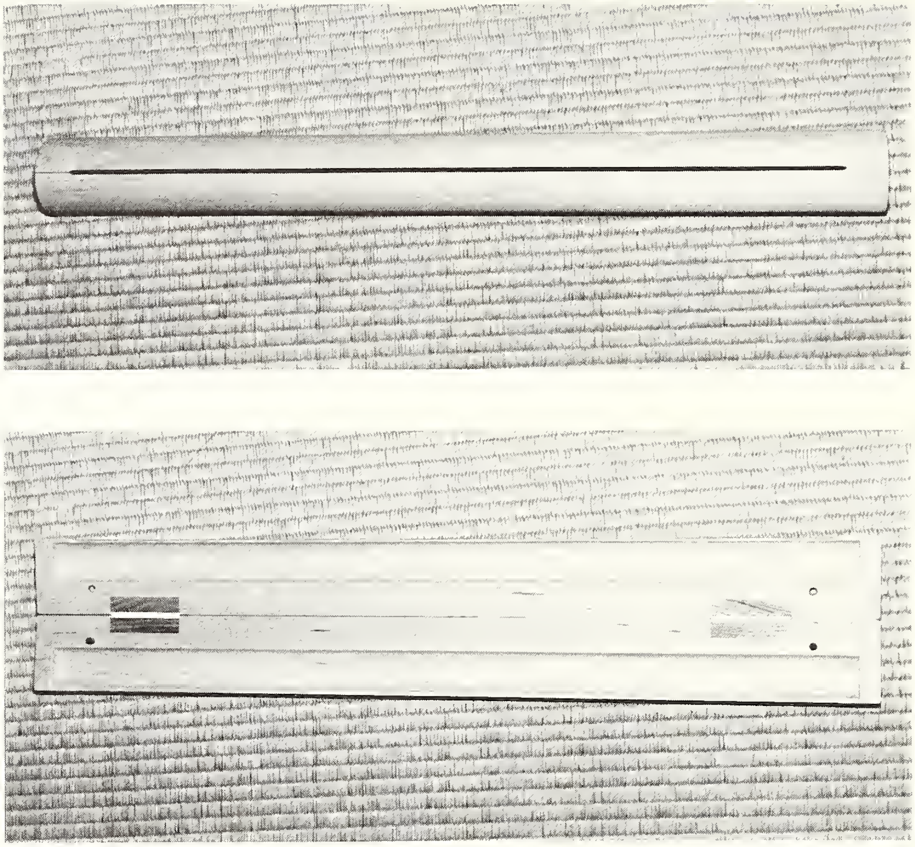

Fig. 15.—Large diameter roller designed to enclose the original roller to give a greater rolling diameter.

In Japan, a recent recommendation has been to roll the scroll on a larger diameter roller placed around the original one, as illustrated in Figure 15.

Certainly, a scroll suffering from cracking and creasing may be remounted by the skilled mounter so that such defects are very well disguised. However, prevention of damage is obviously a much better answer, quite apart from the fact that such restoration skills are only available in certain countries, such as Japan.

PROPER PERIOD OF EXHIBITION

If one accepts the distinction drawn above between a reversible first-stage deformation during a limited exhibition period, and an irreversible second-stage deformation for a longer exhibition period, then there is a definite basis for limiting the periods of exhibition. For example, if second-stage deformation begins after just one year of exhibition, one would have a decisive reason for limiting the exhibition to one year.

In practical terms, we regard the acceptable limit for one exhibition as one month, though it is difficult to present a decisive reason for this. The probable intent of the curator or owner is to fail to detect observable deterioration in the scroll after one exhibition. It is generally known by curators that if one scroll of a pair is exhibited, the other being in storage, then after one month the slightest possible deterioration on the exhibited one can just be detected.[11] As deterioration from light, contact with air, high temperature or high humidity is, roughly speaking, integrated continually over time, limitation of exhibition periods to one month is a cautious approach. For the owner or curator to maximize the life of the art object by a policy of caution is entirely rational, and, since material deterioration cannot be reversed, it is a policy that conservators must sympathize with.

PROPER ENVIRONMENTAL CONDITIONS

As shown above, the Japanese painting has its weak points, especially the facts that the pigment layer has no protective film, the grains being partly exposed, and that the support is not very tough, leading to creasing of the scroll and the danger of tearing in panels. Accordingly, adequate care must be taken over the proper environmental conditions.

If the illumination is limited to proper levels, deterioration depends strongly on relative humidity, and from this point of view a relative humidity of less than 60% is preferable. In dry air, on the other hand, paper, glue and paste become brittle, leading to a greater danger of mechanical damage. The mean relative humidity in Japan over the whole year is somewhat over 70%; if we consider that paintings, and especially panel paintings, will tolerate only a limited departure from the conditions in which they were mounted, it follows that paintings mounted in Japan should not be transferred to a very dry environment. Taking these points into consideration, we believe 55–60% to be the best relative humidity range, but if the humidity can be lowered gradually, and kept constant, the lower limit might well be dropped to 50%. Below 50%, however, is thought to be better avoided for Japanese paintings, especially for panels such as sliding doors and folding screens.

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[11] Mr. Iwatarō Oka (private communication) has recently indicated that he has found second-stage deformation in hanging scrolls exhibited for only one month. Mr. Oka's opinion would therefore limit exhibition periods to something less than this.

A PIGMENT CENSUS OF UKIYO-E PAINTINGS IN THE FREER GALLERY OF ART

By ELISABETH WEST FITZHUGH*

INTRODUCTION

The Freer Gallery Collection includes over 600 paintings and drawings of the *Ukiyo-e* school in Japan, dating from the late 16th to the mid-19th century. Of these paintings, 402 have been examined and a wide selection of the pigments used have been sampled and identified. The technical examination of these paintings, which was begun in 1969, was originally intended as part of a catalogue in which they would be discussed as examples in the history of technology as well as from their art historical aspect.[1] This census of the pigments used on *Ukiyo-e* paintings in the Freer serves to define one aspect of their technological history.

Ukiyo-e works first appeared in the late 16th century during the Momoyama period (1573–1615) and continued to be produced through the Edo period (1615–1868), and into the very early years of the Meiji period (1868–1912). The subject matter of these paintings is the everyday life of the ordinary people of Japan. *Ukiyo-e* literally means pictures (*e*) of the floating or transient world (*ukiyo*). The term can refer to wood-block prints or paintings. Some *Ukiyo-e* artists produced either prints or paintings; many produced both. The paintings are executed on silk and on paper, and are in the form of hanging scrolls (*kakemono*), handscrolls (*makimono*), folding screens (*byōbu*), and drawings or sketches; some of the latter were originally album leaves. All of these types of *Ukiyo-e* painting are represented in the Freer collection. There are a number of wood-block prints in the study collection and a few among the formally accessioned material.[2]

Of the 402 paintings examined, 68 had no color and 19 with color were not sampled. A group of 176 of the remaining 315 paintings were counted as 12 works. The latter included 8 pairs of paintings, each pair being by the same artist, and four groups of paintings each treated as one. These were: a set of 75 drawings by Hiroshige (accession number 04.357); an album of 42 sketches by Hokusai (75.14); 24 drawings by Iwasa Matabei (69.8–69.19 and 70.8–70.19); and a set of 19 drawings by Kawanabe Kyōsai (69.28–69.46). Thus the data on the pigment occurrences came, in effect, from 151 paintings. The information was tabulated on a Hewlett-Packard Programmable Calculator, HP9825A. The accession number, date group, pigment occurrences and identification methods used were entered for each painting. This information could then be retrieved in several ways. A complete listing could be made of the paintings in order of accession number, giving date group, pigments found, and identification method used for each. This listing could also be broken down by date group. In addition, for each pigment, the total number of occurrences, indicating the number of identifications made by each method, could be itemized. Pigment occurrences broken down by group could also be listed.

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[1] Rutherford J. Gettens, "Japanese Paintings: Technical Studies and Conservation at the Freer Gallery of Art," *Conservation and Restoration of Pictorial Art*, N. Brommelle and P. Smith, Editors (London: Butterworths, 1976), pp. 241–252 (Papers presented at the Lisbon Congress, IIC, 1972).

[2] Some pigment identification on Japanese wood-block prints was reported in Nancy Grove, "Appendix" to *Ukiyo-e Prints and Paintings; The Primitive Period (1680–1745)*, by Donald Jenkins, (Chicago: Art Institute of Chicago, 1971) p. 128.

Five dating groups were used for the purposes of this survey. Attribution of each painting to a specific artist, or to a specific dating is not always firm. Sixty-one of the paintings were published in the catalogue of the Freer Gallery 50th Anniversary Exhibition.[3] These and all other paintings acquired since 1954 are considered to have definite attributions. Of the paintings acquired before 1917 (no *Ukiyo-e* paintings were added to the collection between 1917 and 1954), some are firmly dated, but many have only the attribution made when first accessioned. The question mark (?) following the date or artist's name in Table 1 does not necessarily mean that the dating is questionable, but only that adequate evidence for attribution from recent art historical research is at present lacking.

Pigment identification was carried out chiefly by microscopic means. Samples were always taken from areas which showed no indication of recent overpaint; in any case, there is little overpainting on these paintings. The sampling and mounting techniques have been described.[4] In brief, the optical appearance of the pigment, mounted in Canada balsam ($n = 1.53$) or Aroclor 5442 ($n = 1.66$) on a microscope slide, was observed in reflected and then in transmitted (plane polarized) light, and between crossed polars, at magnification usually up to × 500, but sometimes up to × 1000 (the latter with an oil immersion lens). The description of each pigment which follows summarizes the optical characteristics. When considered advisable confirmatory chemical tests were made under the microscope to determine the effect of acid or alkali and to test for the presence of a particular element.[5] The notes to Table 1 indicate which of the variety of possible tests available were used. A limited number of pigments were identified by the X-ray diffraction powder method. These methods have certain limitations, particularly in the case of organic colorants, where sometimes only general observations are possible. For this reason, the descriptions of the pigments which follow, and the notes to Table 1, are intended to indicate what criteria were used for identification.

Not all pigments were necessarily sampled from each painting. In most cases a complete sampling of all colors was carried out. Some paintings, especially the drawings and sketches, executed in a thin wash, did not have sufficient pigment for extensive microscopy. In other cases only a preliminary sampling was made.

Two classes of pigments have not been included in this study. Carbon pigments are an important element in all these paintings, but because of their small particle size they are better studied by methods such as scanning electron microscopy.[6] Metal leafs and powders, of gold, silver, and copper alloy, all of which are used, were also not included.

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[3] Harold P. Stern, *Freer Gallery of Art, Fiftieth Anniversary Exhibition, I. Ukiyo-e Painting*, (Washington, D.C.: Smithsonian Institution, May 2, 1973), 319 pp. (catalogue of the exhibition).

[4] Gettens "Japanese Paintings."

[5] See references for individual pigments, and also Joyce Plesters, "Cross-sections and Chemical Analysis of Paint Samples", *Studies in Conservation*, vol. 2, (1956), pp. 110–157.

[6] John Winter, "Preliminary Investigations on Chinese Ink in Far Eastern Paintings," *Archaeological Chemistry*, Curt Beck, Editor. (Washington, D.C.: American Chemical Society, 1974), pp. 207–225. (Symposium sponsored by Division of the History of Chemistry, A.C.S., Dallas, Texas April 9–10, 1973).

PIGMENT PROPERTIES

Eighteen different classes or types of pigments have been identified and are summarized below.

Two white pigments were found on these paintings. Shell white in the Far East is a form of calcium carbonate, $CaCO_3$, made by grinding sea shells, chiefly oyster shells.[7] The Japanese name is *gofun*. Particles of shell white as observed through the microscope are lath-shaped, fibrous, variable in size, and highly anisotropic; refractive indices are $\epsilon = 1.49$, $\omega = 1.66$.

Lead white, *empaku* in Japanese, is artificially made basic lead carbonate, $PbCO_3 \cdot 2Pb(OH)_2$. Under the microscope it is generally very finely divided, of uniform size and anisotropic, with high refractive indices $\epsilon = 1.94$, $\omega = 2.09$.[8]

Four types of red pigment were found. Vermilion, Japanese *shu* or *shin-sha*, is red mercuric sulfide, HgS. The natural material is finely ground mineral cinnabar. The two types of synthetic material are made by the dry process and the wet process. Wet process vermilion is usually very uniform and finely divided. Ground cinnabar and dry process vermilion are both more uneven in particle size and difficult to differentiate from each other. It appears that either dry process or natural cinnabar was used on these paintings, because of the cleavage planes observed and the large size of the fragments. Dry process vermilion is stated to have been in wide use in the Edo period.[9] Vermilion in transmitted light is a clear cherry red; it is highly anisotropic, yellow to orange between crossed polars, with high refractive indices ($\omega = 2.819$, $\epsilon = 3.146$). Particles of ground cinnabar or dry process vermilion often have a fractured look, and are hexagonal in shape, reflecting the fact that cinnabar belongs to the hexagonal crystal system.[10] Vermilion was sampled from the painting proper, not from the seals.

Red lead, Japanese *entan* or *tan*, is artificially made lead tetroxide, Pb_3O_4. Microscopically it appears as tiny rounded grains, red to orange in transmitted light, weakly anisotropic with high refractive index ($n = 2.42$). Characteristic blue-green interference colors are seen between crossed polars.[11]

Red earth pigments, Japanese *beni-gara* or *bengara*, derive their color from hematite, α-Fe_2O_3, the main colorant in a variety of natural and artificial pigments, which often occur as complex mixtures with other materials such as clay minerals and mineral

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[7] Rutherford J. Gettens, Elisabeth West FitzHugh and Robert L. Feller, "Calcium Carbonate Whites," *Studies in Conservation*, vol. 19 (1974), pp. 157–184.

[8] Rutherford J. Gettens, Hermann Kühn and W. T. Chase, "Lead White," *Studies in Conservation*, vol. 12 (1967) pp. 125–139.

[9] Hachirō Oguchi, "Scientific Investigation on Color Materials in Japanese Painting," *Bulletin of the Faculty of Fine Arts, Tokyo University of Arts*, no. 5 (1969), pp. 27–81 (In Japanese with English summary).

[10] Rutherford J. Gettens, Robert L. Feller, and W. T. Chase, "Vermilion and Cinnabar," *Studies in Conservation*, vol. 17 (1972), pp. 45–69.

[11] Elisabeth West FitzHugh, "Red Lead and Minium," Monographs on ten artists' pigments, Robert L. Feller, Editor, to be published by the National Gallery of Art, Washington, D.C. and the National Endowment for the Arts. See also Esper S. Larsen and Harry Berman, *The Microscopic Determination of the Non-opaque Minerals*, U.S. Department of the Interior, Geological Survey, Bulletin 848 (Washington, D.C.: U.S. Government Printing Office, 1934), p. 216.

Table 1
Pigments Identified in Individual Paintings

Abbreviations: hg = hanging scroll, hd = handscroll, sc = screen, dr = drawing or sketch, s = silk, p = paper, m = identified by microscopic appearance, c = identified by chemical microscopy (see footnote to table), x = identified by x-ray diffraction.

Accession number	Artist	Date	Painting type	Support	White		Red				Yellow			Green		Blue					Brown	
					Shell white	Lead white	Vermilion	Red lead	Red earths	Organic red	Orpiment	Yellow earths	Organic yellow	Malachite	Copper greens	Azurite	Smalt	Ultramarine	Indigo	Prussian blue	Brown earths	Organic brown
Group 1: Late 16th to mid 17th century																						
69.8–69.19 (70.8–70.19)**	Iwasa Matabei	1578–1650	dr	p	m		m	m						m		m						
97.4	Unknown	17th?	hg	p	m		mc						mc	m		m					mc	
01.173	Unknown	1st quarter 17th	sc	p	mc		m							mc		m						
02.242	Unknown	late 16th–early 17th	sc	p	m		mc							m		m					m	
03.100	Unknown	late 16th–early 17th	sc	p	m		m							m		m					m	
03.208	Unknown	early 17th?	sc	p	mc		m						mc	m		m					m	
04.53	Unknown	17th	hg	p	m		mc					m		mc							mc	
04.352	Unknown	17th?	hg	p	mc		mc							mc		mc					m	
07.135	Unknown	17th?	sc	p	mc		m	mc						mc		m						
17.203	Unknown	17th	sc	p			m							m		m			mc			m
59.8	Unknown	mid-17th	sc	p			mc							mc			m					
65.22–65.23	Unknown	16th	sc	p	mc		mc	mc						mc		mc						
72.8–72.9	Unknown	17th	sc	p	m		m	m					mc	m		m			m		mc	
Group 2: Mid 17th to mid 18th century																						
98.505	Bunkaku	early 18th	sc	p	m			m					mc	mc								
98.428	Hanabusa Itchō?	1652–1724	hg	p	m		m			m				m			m					mc
03.47 (03.48)	Hanabusa Itchō	1652–1724	sc	p	mc		m			mc			mc	m		m			mc		mc	
03.108	Hanabusa Itchō?	1652–1724	hg	s	m		m			m									m			
04.136	Hanabusa Itchō	1652–1724	hd	p	mc		m	mc		mc			mc	m					mc			
04.138	Hanabusa Itchō?	1652–1724	hd	s	m		m			m			mc	m		m			mc			
04.387	Hanabusa Itchō?	1652–1724	hg	s	m														m			
04.388	Hanabusa Itchō?	1652–1724	hg	s			m															
07.657	Hanabusa Itchō?	1652–1724	dr	p			m															
98.7	Hishikawa Morofusa	fl. 1685–1703	hg	p	m		m									m						
98.76	Hishikawa Moronobu?	d. 1694	hg	s	m		mc	mc							mc	m						
06.266–06.267	Hishikawa Moronobu?	d. 1694	sc	p	m		m	mc						m		mc					m	
98.12	Hishikawa Moroshige?	fl. 1678–1698	hg	s	m		m	mc						m								
98.114	Hishikawa Moroyasu	fl. early 18th	hg	p	m		m													mc		mc
01.15	Kaigetsudō Ando	early 18th	hg	p	mc		m	m		m			mc		mc				mc		mc	
03.59	Kaigetsudō Ando	early 18th	hg	p	m		m						mc	mcx			m		mc			mc
03.73	Kaigetsudō Ando	early 18th	hg	p	mc		m										m				m	
66.2	Kaigetsudō Ando	early 18th	hg	p	mc		mc										m		mc		mc	
01.9	Miyagawa Chōki	fl. mid 18th	hg	p	mc		m						mc	m					mc			mc
98.92	Miyagawa Chōshun?	1683–1753	sc	s	m		m							m		m						
98.101	Miyagawa Chōshun	1683–1753	hg	p	mc		m						mc				m		m			mc
98.112	Miyagawa Chōshun?	1683–1753	hg	s	mc		m	m		mc				m		m			mc			

98.429	Miyagawa Chōshun	1683–1753	hg	s	mc		m							m					mc	mc		mc
03.134	Miyagawa Chōshun?	1683–1753	hg	p	mc		m			m				mcx			m		mc			m
03.135	Miyagawa Chōshun?	1683–1753	hg	s	mc		m	m						m			m		mc	mc		mc
04.140	Miyagawa Chōshun?	1683–1753	hd	p	m		m	mc		m			mc	m		m			mc		mc	mc
59.12	Miyagawa Chōshun	1683–1753	hd	p	m		m	mc		mc			mc	m		m			mc		mc	mc
97.2	Nishikawa Sukenobu	1671–1751	hg	p	m		m															
98.100	Okumura Masanobu	1686–1764	hg	s	mc		m	mc	m				mc	m		m			mc			
98.119	Okumura Masanobu	1686–1764	hg	s	mc		m	mc	mc					m		m			mc			
02.99	Okumura Masanobu	1686–1764	hg	p	mc		m	m					mc						mc			
02.250	Okumura Masanobu	1686–1764	hg	p	mc		mc		mc	m	mcx								mc			
98.14	Torii Kiyonobu I	1664–1729	hg	p	m		m	m							mcx		m		mc		m	
00.25–00.26	Unknown	17th–18th	sc	p	m		m							mc		m					m	
00.112	Unknown	18th	hg	p	mc		m								mcx		m				mc	
01.12	Unknown	mid 18th?	hg	s	mc		m			mc			mc						mc		mc	
01.13	Unknown	17th–18th?	hg	p	mc		m						mc		mc		m		mc		mc	mc
01.28	Unknown	2nd quarter 18th	hg	p	m		m										m				m	mc
05.96	Unknown	late 17th	hg	s	m			mcx	mcx					m			m					
Group 3–2nd quarter to end of 18th century																						
98.99	Isoda Koryūsai?	fl. 1764–1788	hg	s	m		m	mc		m			mc	mc		m						
98.10	Katsukawa Shunshō?	1726–1792	hg	s	m		m		mc					m					m			
98.104	Katsukawa Shunshō?	1726–1792	hg	s	m		m		mc					m	mc	m			mc			
98.115	Katsukawa Shunshō?	1726–1792	hg	s	mc		m			m			mc	m					mc			
98.136	Katsukawa Shunshō?	1726–1792	hg	s	m		mc			m				m	mc	mc	m					
98.426	Katsukawa Shunshō	1726–1792	hg	s	mc		m			m			mc	mcx		m			mc			
04.191	Katsukawa Shunshō?	1726–1792	hg	p	m		m	mc											m			
05.271	Katsukawa Shunshō?	1726–1792	hg	s	mc		m		mc		m		mc	m		m			mc			
05.309 (05.308)	Katsukawa Shunshō	1726–1792	hg	s	m		m		mc	m	m				mc				mc			
98.98	Kawamata Tsunemasa?	active 1716–1744	hg	s	m		m		m				m	m		m	m		m			
98.109	Miyagawa Shunsui (Katsukawa Shunsui)	active 1744–1764	hg	p	m		m		mc	m				m			m					
01.5	Miyagawa Shunsui (Katsukawa Shunsui)	active 1744–1764	hg	p	m		m						mc	m		m			mc		m	
06.6	Miyagawa Shunsui (Katsukawa Shunsui)	active 1744–1764	hg	p	mc		m	m	mc			mc		m					mc	mc		
98	Suzuki Harunobu?	1724–1770	hg	p	m		m	m		m									mc		m	
01.166	Suzuki Harunobu	1724–1770	hg	p	mc		m	mc		m			mc	mcx		m	m		mc		m	mc
06.48	Suzuki Harunobu?	1724–1770	hg	p	m		m			m			mc				m		mc			
61.25	Tsukioka Settei	1710–1786	hg	p			mc															
98.425	Unknown	late 18th?	hg	s	mc		mc	m		m				m					mc			
03.66	Unknown	late 18th?	hg	p	mc		m						mc		mc		m		mc		mc	mc
03.69	Unknown	18th?	hg	s	m		m		mc			mc		m			m					
Group 4–2nd quarter of 18th through first quarter of 19th century																						
98.93	Hosoda Eishi?	1756–1829	hg	s		mc	m	m		mc			mc			m						
98.117	Hosoda Eishi?	1756–1829	hg	s		mc	m	mc		m			m	m		m			mc			
98.500	Hosoda Eishi?	1756–1829	hg	s	m		m	m		m			mc	mcx		mc						mc
05.294	Hosoda Eishi?	1756–1829	hg	s	m		m	m		m				mcx		m			mc	mc		
06.11	Hosoda Eishi?	1756–1829	hg	s	mc	mc	m	m		m				mcx		m				mc		mc
57.5 (57.6)	Hosoda Eishi	1756–1829	hg	s		mc	m		mc	m			mc	mc		m			mc			
57.7	Hosoda Eishi	1756–1829	hg	s				m											mc	mc		mc
74.16–74.17	Jogen?	ca. 1773–1824	hd	p	m		m			m			mc	m		m			mc			
03.56	Katsukawa Shunchō	fl. 1780–1795	hg	s	m		m		m					m		m			mc			

Table 1 (*continued*)

Abbreviations: hg = hanging scroll, hd = handscroll, sc = screen, dr = drawing or sketch, s = silk, p = paper, m = identified by microscopic appearance, c = identified by chemical microscopy (see footnote to table), x = identified by x-ray diffraction.

Accession number	Artist	Date	Painting type	Support	White		Red				Yellow			Green		Blue					Brown	
					Shell white	Lead white	Vermilion	Red lead	Red earths	Organic red	Orpiment	Yellow earths	Organic yellow	Malachite	Copper greens	Azurite	Smalt	Ultramarine	Indigo	Prussian blue	Brown earths	Organic brown
03.132	Katsukawa Shunchō?	fl. 1780–1795	hg	s	m		m		m	m	mc			mc		m			m			
99.18	Katsukawa Shun'ei	1762–1819	hg	s	mc		m		mc		mc			m					mc			
98.5	Katsukawa Shungyo?	late 18th–early 19th	hg	s	mc		m									mc						
98.423	Katsukawa Shunkō	1743–1812	hg	p	m		m	m		mc	mx					m	m				mc	
98.60	Kitagawa Utamaro	1754–1806	hg	p	m		m					mc		m		m			mc			
99.16	Kitagawa Utamaro?	1754–1806	hg	s										m								
03.54	Kitagawa Utamaro	1754–1806	hg	p	m		m							mc			m		mc			
98.120	Kitao Masanobu?	1761–1816	hg	s	mc		m	m		m			mc	m		m			mc			
01.11	Kitao Shigemasa?	1739–1820	hg	s	m		m		mc	m				m		m						
02.90	Kitao Shigemasa?	1739–1820	hg	s	mc		m			m				m					mc			
02.253	Kitao Shigemasa?	1739–1820	hg	s	m		m			m				m		m					mc	
03.64	Kitao Shigemasa?	1739–1820	hg	s	m		m	m		mc									mc			
03.76	Kitao Shigemasa?	1739–1820	hg	s	mc		m			m					mc				mc			
98.51	Kubo Shunman?	1757–1820	hg	s	m		m	mc		m				m		m						
57.2	Kubo Shunman	1757–1820	hg	s	m		m	m		mc			mc	m			m		mc			
98.96	Shiba Kōkan	1747–1818	hg	s	mc		m							mc			m		mc			
62.19	Shorakusai	late 18th–early 19th	hd	p	mc											m						
98.13	Torii Kiyonaga	1752–1815	hg	s	mc		m			m				m					mc			
01.100	Torii Kiyonaga	1752–1815	hg	s	mc		m			m							m		mc			
02.101	Torii Kiyonaga	1752–1815	hg	s	mc		m			m			mc		mc				mc			
96.93	Akizuki Tōrin III?	ca. 1743–1820	hg	s	m		m												m			
98.75	Utagawa Toyoharu	1735–1814	hg	s	mx		mc	mc						mx		m					m	
98.102	Utagawa Toyoharu?	1735–1814	hg	s	m		m	mc		m			mc	mc			m		mc		mc	
98.113	Utagawa Toyoharu	1735–1814	hg	s	m		m		mc	mc				m	mc	m			mc		mc	mc
98.15	Utagawa Toyohiro?	1773–1828	hg	s	m		m	mc					m			m						
98.94	Utagawa Toyohiro?	1773–1828	hg	p	mc		m		m	mc	mc			mc	mc							
98.108	Unknown	18th–19th?	hg	s	m		m				m					m			mc		m	
Group 5–end of 18th to late 19th century																						
03.63	Andō Hiroshige	1797–1858	hg	s	m		m			m				m		m	m		mc			mc
04.357	Andō Hiroshige	1797–1858	dr	p	m		m	m		m			mc	m		m			mc	mc	mc	
03.105	Andō Hiroshige	1797–1858	hg	s	m		m			m				m		m					mc	
98.123	Hiroshige II?	1826–1869	hg	s	m										mcx				mc			
98.124	Hiroshige II?	1826–1869	hg	s																mc		
98.125	Hiroshige II?	1826–1869	hg	s			m															
98.126	Hiroshige II?	1826–1869	hg	s	m					m				mcx						mc	mc	
99.17	Hiroshige II?	1826–1869	hg	s									m					mc				
03.97	Hiroshige II?	1826–1869	hg	s	m		m			mc				m								
03.106	Hiroshige II?	1826–1869	hg	s	m				mc				m					m		m		
03.145	Hiroshige II?	1826–1869	sc	s	m		m	m						m				m		mc	mc	

03.146	Hiroshige II?	1826–1869	sc	s						m			mc	m				mc		mc	m
05.234	Hiroshige II?	1826–1869	hg	s	m		m						mc	m		m					m
98.8	Gatukei (Harunobu)?	d. 1868	hg	s	m		m		m						mc					mc	
98.419	Hokuun?	fl. early 19th	hg	s	m		m	m	mc	m	mc				mc				mc		
98.74	Katsushika Hokusai?	1760–1849	hg	s	mc		m	mc		m									mc	mc	
98.95	Katsushika Hokusai?	1760–1849	hg	p	m																
98.97	Katsushika Hokusai?	1760–1849	hg	p											mc						
98.103	Katsushika Hokusai?	1760–1849	hg	s	m		m														
98.105	Katsushika Hokusai?	1760–1849	hg	s	m		m						mc						mc		
98.106	Katsushika Hokusai?	1760–1849	hg	s	mc		m			mc			mc						mc		
98.107	Katsushika Hokusai?	1760–1849	hg	p	m		m			mc					mc					mc	
98.110	Katsushika Hokusai	1760–1849	hg	s	mc										mc					mc	
98.111	Katsushika Hokusai?	1760–1849	hg	s			m				mc								m		
03.2	Katsushika Hokusai?	1760–1849	hg	s	mc		m		m	mc	mc				mc	m			mc		
04.73	Katsushika Hokusai	1760–1849	dr	p	m											m					
04.134	Katsushika Hokusai?	1760–1849	hg	s	mc		m	m		mc	mcx				mc				m		
04.207	Katsushika Hokusai	1760–1849	dr	p			m														
04.208	Katsushika Hokusai	1760–1849	dr	p	m		m														
04.212	Katsushika Hokusai	1760–1849	dr	p						m											
04.214	Katsushika Hokusai	1760–1849	dr	p					m						mc						
04.215	Katsushika Hokusai	1760–1849	dr	p											mc						
04.216	Katsushika Hokusai	1760–1849	dr	p			m														
04.218	Katsushika Hokusai	1760–1849	dr	p																mc	
04.219	Katsushika Hokusai	1760–1849	dr	p					m												
04.221	Katsushika Hokusai	1760–1849	dr	p															mc		
04.222	Katsushika Hokusai	1760–1849	dr	p						m											m
04.224	Katsushika Hokusai	1760–1849	dr	p															m		
04.225	Katsushika Hokusai	1760 1849	dr	p			m												mc		
04.428	Katsushika Hokusai	1760–1849	dr	p					mc												
06.50	Katsushika Hokusai?	1760–1849	hg	s	m		m	m	mc					m							
75.14	Katsushika Hokusai	1760–1849	dr	p	mcx						mcx									mc	
69.28–69.46	Kawanabe Kyōsai (Gyōsai)	1831–1889	dr	p	m		m												m		

* CHEMICAL MICROSCOPY. If no reference is given, the tests described are in the *Studies in Conservation* articles on individual pigments already cited. **Shell white:** Effervescence in dil. HCl. Test for calcium with H_2SO_4. **Lead white:** Dil. HNO_3 causes effervescence and formation of lead nitrate. Test for lead with potassium iodide. **Vermilion:** Insoluble conc. & dil. HCl & HNO_3. Soluble aqua regia. Soluble hydriodic acid. Test for mercury with double thiocyanate test. **Red lead:** Formation of lead nitrate with dil. HNO_3. Test for lead as with lead white.[28] **Red earths:** Insoluble conc. & dil. HCl. Soluble aqua regin. Insoluble hydriodic acid (differentiates from vermilion). Test for iron with potassium ferrocyanide.[29] **Organic red:** 5% NaOH causes violet color; subsequent addition of dilute HCl sometimes produces an orange color.[30] **Orpiment:** Test for arsenate with ammonium molybdate.[31] **Yellow earths:** Insoluble conc. & dil. HCl. Soluble aqua regia. Test for iron as with red earths. **Organic yellow:** 5% NaOH causes formation of an orange color if gamboge is present.[32] In 34 out of 40 tested in this way a definite orange color developed. **Malachite:** Usually effervescence with dil. acids. Test for copper with potassium ferrocyanide. **Copper greens:** All tested positive for copper, as with malachite. **Azurite:** Usually effervescence with dil. acids. Test for copper, as with malachite. **Smalt:** Chemical microscopy difficult because of insolubility. Microscopic recognition usually considered sufficient.[33] **Ultramarine:** Dil. HCl destroys the blue color, producing odor of H_2S. **Indigo:** Decomposed by dil. HNO_3 to form yellow isatin. Unaffected by 5% NaOH.[34] **Prussian blue:** Unaffected by dil. HCl and HNO_3. 5% NaOH destroys blue color and subsequent addition of dilute HCl causes its re-formation.[35] **Brown earths:** Behavior as with yellow earths. **Organic brown:** Concentrated H_2SO_4 and 5% NaOH both cause formation of a brown stain.

** Accession numbers in parentheses: these paintings were not sampled, and are either one of pair, or in a group of paintings by the same artist.

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[28] Joyce Plesters, "Cross-sections," p. 143.

[29] Emile Monnin Chamot and Clyde Walter Mason, *Handbook of Chemical Microscopy*, Vol. II (New York: John Wiley & Sons, 1931), p. 238.

[30] Gettens and Stout, *Painting Materials*, pp. 110, 127.

[31] M. N. Short, *Microscopic Determination of the Ore Minerals*. U.S. Department of the Interior, Geological Survey, Bulletin 914, 2nd edition (Washington, D.C.: U.S. Government Printing Office, 1940), pp. 209, 284, Plates C & D.

[32] Gettens and Stout, *Painting Materials*, p. 115.

[33] Mühlethaler and Thissen, "Smalt."

[34] Gettens and Stout, *Painting Materials*, p. 120.

[35] Plesters, "Cross-sections," p. 137.

silicates.[12] Hematite itself is a clear transparent red when viewed through the microscope, anisotropic, orange to dark red between crossed polars, with refractive indices close to those of vermilion ($\epsilon = 2.94$, $\omega = 3.22$).[13] From optical appearance alone it is not always easy to distinguish from vermilion. Finely divided red earth occurs in a range of uniformly small particle sizes, so fine that sometimes it appears only as a rosy stain.

An organic red pigment appears in these paintings as pink or purplish-pink. Under the microscope in transmitted light it appears as a stain, with no particulate structure. There are three types of red dye which may have been used on these paintings. One is safflower red, which is derived from the petals of safflower, *Carthamus tinctorius* L. (Japanese *benibana*). The red constituent is carthamic acid or carthamin. The second is madder. Western madder, *Rubia tinctorum* L., contains alizarin and purpurin as coloring constituents, while Japanese madder, *Rubia akane* Nakai contains purpurin alone.[14] The third includes cochineal, kermes or lac dye (Indian lake), all of which are derived from insects; the coloring materials are all anthroquinone derivatives.[15] *Beni* is the Japanese name for safflower red. *Shiko* refers to lac dye. *Enji* appears to refer to one or more red dyes; the exact meaning of the word is not known. Recently a reddish purple colorant identified by name as *enji* on a scroll dated to 1695 was identified by spectrophotometry as laccaic or carminic acid.[16] Literary evidence indicates that cochineal was known in Japan by 1800.[17]

Three yellow colorants were found. Orpiment, in Japanese *shiō*, *kiō* or *sekiō*, is the naturally occurring mineral arsenic sulfide, As_2S_3. Particles are usually coarse, of limited transparency, and their foliated, micaceous structure can be seen on microscopic examination. The mineral is highly anisotropic, the refractive indices are high ($\alpha = 2.4$, $\beta = 2.81$, $\gamma = 3.02$).[18] and green to red interference colors can be seen between crossed polars. In reflected light the appearance is resinous or waxy.

Yellow earth pigments derive their principle color from .the mineral goethite, FeO(OH). It is the coloring material in yellow ochre, *ōdo* in Japanese, which also contains clay minerals and silica. Microscopically semi-opaque pale yellow and brown particles can be seen in most yellow earths; the refractive indices are $\alpha = 2.260$; $\beta = 2.393$; $\gamma = 2.398$.[19]

An organic yellow pigment is possibly gamboge, Japanese *tō-ō* or *kusa-shiō*, a gum resin obtained from trees of the genus *Garcinia*. In amounts obtainable from these paintings, the microscopic appearance of this pigment is only a yellow stain.

Two general types of green pigment were found. Malachite is a green natural copper mineral, a basic copper carbonate $Cu_2CO_3(OH)_2$, in Japanese *rokushō* or *iwa rokushō*. In transmitted light, the particles are pale green, almost colorless when small, with squarish fracture, sometimes striated or fibrous, highly anisotropic, with high refractive indices ($\alpha = 1.655$; $\beta = 1.875$; $\gamma = 1.909$).[20] A green copper-containing pigment, which was identified as malachite by X-ray diffraction, but did not have the typical microscopic appearance of malachite, was found on a few of these paintings. The particles are more rounded than one would expect of ground mineral malachite but they are not the typical spherulitic particles of artificial malachite (green verditer), which show definite crosses when viewed between crossed polars.

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[12] Rutherford J. Gettens and George L. Stout, *Painting Materials* (New York: Dover, 1966), p. 122.

[13] Willard Lincoln Roberts, George Robert Rapp, Jr., and Julius Weber, *Encyclopedia of Minerals* (New York: Van Nostrand Reinhold, 1974), p. 266.

[14] Kazuo Yamasaki, private communication.

[15] K. S. Brown, Jr., "The chemistry of aphids and scale insects," *Chemical Society Reviews*, vol. 4 (1975), pp. 263–288.

[16] Ei-ichi Taguchi and Mamiko Taguchi, "Spectrophotometric identification of coloring materials, especially of organic pigments, and combined mixed colors—with reference to the pigments used in the scroll, 'Genji-monogatari 54-jo Emaki' of the Edo period," *Kobunkazai no Kagaku* (*Scientific Papers on Japanese Antiques and Art Crafts*), no. 20/21 (1977), pp. 18–37. In Japanese, English abstract. Additional information supplied by K. Yamasaki.

[17] Kazuo Yamasaki, private communication.

[18] Roberts, Rapp and Weber, *Encyclopedia of Minerals*, p. 450.

[19] *Ibid.*, p. 240.

Copper greens other than malachite are encountered in this series of paintings. Since our knowledge concerning these greens is incomplete, they have been grouped together. They often have the superficial appearance of granular mineral malachite on the painting. Microscopic appearance varies, but all give a positive test for copper. Some of these greens have been identified by X-ray powder diffraction. Emerald or Paris green, copper aceto-arsenite, was found on a painting by Hiroshige (1797–1858). This artificial pigment was first made in Germany in 1814. Another copper green found was one of the dimorphic basic copper chlorides, atacamite or paratacamite, $Cu_2(OH)_3Cl$. There are other copper greens which are as yet unidentified. To date, there is no evidence from X-ray diffraction that any of these greens are verdigris (basic copper acetate).

Five different blues are used on these paintings. Azurite is a natural copper mineral, a basic copper carbonate, $Cu_3(OH)_2(CO_3)_2$, in Japanese *gunjō* (or *iwa gunjō* to differentiate it from ultramarine). In transmitted light particles are irregular and fractured, pleochroic and anisotropic. Larger particles are deep blue with greenish undertone and small particles are pale blue; refractive indices are $\alpha = 1.730$; $\beta = 1.758$; $\gamma = 1.838$.[21]

Smalt is an artificial pigment, a coarsely-ground potassium-rich glass which has been colored with cobalt oxide, in Japanese *hana-konjō*. Microscopically, particles vary from pale blue, sometimes purplish, to bright azurite blue, are isotropic and transparent, and show square and angular corners and conchoidal fracture; refractive index varies from $n = 1.46$ to 1.55.[22]

Natural ultramarine is the powdered mineral lapis lazuli, a complex sodium aluminum silicate. Synthetic ultramarine of the same composition was first made in France in 1828. The Japanese name, *gunjō*, is sometimes also used for azurite. Microscopically ultramarine is isotropic, with low refractive index ($n = \sim 1.5$), and deep purplish blue in transmitted light. The particles disappear when viewed between crossed polars. The natural material is irregular in particle size and contains calcite and other mineral impurities. Synthetic ultramarine particles are finely divided, somewhat rounded, and regular in size.[23]

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[20] Rutherford J. Gettens and Elisabeth West FitzHugh, "Malachite and Green Verditer," *Studies in Conservation*, vol. 19 (1974), pp. 2–23.

[21] Rutherford J. Gettens and Elisabeth West FitzHugh, "Azurite and Blue Verditer," *Studies in Conservation*, vol. 11 (1966), pp. 54–61.

[22] Bruno Mühlethaler and Jean Thissen, "Smalt," *Studies in Conservation*, vol. 14, (1969), pp. 47–61.

[23] Joyce Plesters, "Ultramarine Blue, Natural and Artificial," *Studies in Conservation*, vol. 11 (1966), pp. 62–91.

Indigo, Japanese *ai*, is an organic pigment obtained from several species of plants; in Japan the plant is *Polygonum tinctorium*. The microscopic appearance of indigo is usually that of a stain; sometimes tiny opaque particles are visible.

Prussian blue is an artificial blue pigment first made in Germany in 1704, ferric ferrocyanide, $Fe_4(Fe(CN)_6)_3$. Sometime during the 18th century it is said to have supplanted indigo in Japan.[24] The Japanese name is *konjō* or *berensu*. The pigment is so finely divided that through the microscope by transmitted light it appears as a non-particulate green-blue stain.

Two brown pigments appear to have been in use by *Ukiyo-e* artists. Brown iron-bearing earth pigments exist that are similar in composition to the red iron oxide colors described above; some may contain manganese. Hematite particles can sometimes be seen.[25]

An organic brown pigment, which has not to date been characterized, was found on twenty of these paintings. Microscopically it appears only as a non-particulate brown stain. Tests for iron are negative. Both 5% NaOH and concentrated H_2SO_4 cause this brown color to go to a brown stain. The behavior with NaOH is typical of Van Dyke brown, but the appearance of these pigment particles is not typical of European Van Dyke browns based on lignite-humus type deposits.[26] Nor does it appear to be a discolored red dye, from evidence at present available.

PIGMENT OCCURRENCES

The pigments found on each painting are listed in Table 1. A few comments follow on the frequency of use of the individual pigments.

Shell white occurred on 85–95% of the paintings in Groups 1 through 4 and on 58% of those in Group 5.

The four occurrences of lead white reported here are all on paintings either by or attributed to Hosoda Eishi (1756–1829).

Vermilion is the most common pigment on the paintings under discussion here; it was found on 92–100% of groups 1–4, but only in 53% of those in Group 5.

Red lead was found on 31–39% of the paintings in groups 1 and 4, and on 14% of those in Group 5.

Red earth pigments did not occur in Group 1, and they were found on 10% of the paintings in Group 2. Their use is most common in Group 3 (42%) and lower (19%) in both Groups 4 and 5.

It appears from chemical microscopy that more than one organic red was used on these paintings. No significance can at present be ascribed to the variation from no occurrences in Group 1 up to 64% in Group 4, since we do not yet know which organic red or reds were in use.

Orpiment was found on only 13 of these paintings. It was not found in Group 1, was rare in Group 2 (2.5%) and frequency of occurrence in the later paintings varied from 11–14%.

Yellow earths were rare on these paintings; only four examples were found, one in Group 1, two in Group 3, and one in Group 4.

An organic yellow pigment, possibly gamboge, occurred rather commonly throughout these paintings, varying from 23–42% in Groups 1 to 4, and being less common (16%) in Group 5.

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[24] C. Schraubstadter, *Care and Repair of Japanese Prints*, (New York: Raiko Art Corp. and Asian Conservation Laboratory, 1978), p. 5. Reprint of 1948 edition with addendum by Doanda Randall.

[25] Gettens and Stout, *Painting Materials*, p. 167.

[26] Robert L. Feller, private communication.

Malachite was very common on these *Ukiyo-e* paintings at all dates, being used on 100% of Group 1, 50–74% in Groups 2–4, and 21% of Group 5.

The copper greens, which may have been used to some extent as a substitute for malachite, were not found on any of the paintings in Group 1, and varied from 11 to 23% in the later paintings.

Azurite was especially common at the beginning of the period, being used on 85% of the paintings in Group 1, on 30 to 58% of those in Groups 2 to 4, and 14% of the paintings in Group 5.

Smalt is rare on the early and late *Ukiyo-e* paintings in this series. It was in most common use, 30–32%, from the mid-17th to the end of the 18th century (Groups 2–4).

Synthetic ultramarine was found on four paintings either by Hiroshige II (1826–1869) or attributed to him.

An indigo-type dye was not common on early *Ukiyo-e* paintings, but the evidence from this investigation suggests that it was widely used from the mid-17th to the beginning of the 19th century. (60–74% in Groups 2–4). In Group 5 it occurred on 33% of the paintings.

Prussian blue is rare on these *Ukiyo-e* paintings up to the end of the 18th century. From the end of the 18th century it is more common, occurring on 28% of the paintings in Group 5.

Brown earth pigments were quite common on early *Ukiyo-e* paintings in this series, occurring on 54% of those in Group 1. They were in steady use, although less common, later in the period, varying from 17 to 33%.

The organic brown was most common from the mid 17th to the mid 18th century (Group 2), when it occurred on 30% of the paintings; it was found more rarely throughout the rest of the period.

CONCLUSION

In conclusion, it is apparent that a number of pigments were found in this study to be present throughout the period of *Ukiyo-e* painting. Shell white, vermilion, red lead, an organic yellow, malachite and azurite were all widely used. What appears to be a decline in their use by the 19th century may only reflect the fact that fewer colors were used on many of the paintings. Artists such as Hokusai tended to use colors much more sparingly than some of the earlier painters. Thus, the lower figures for Group 5 may represent a sampling problem inherent in the identification methods used here, rather than an indication of the prevalence of these pigments.

The red and brown earth pigments were in fairly steady use, and the fluctuation in their occurrence throughout the period does not seem to suggest any definite trend. No red earths were found in the earliest paintings, but since very few were examined in Group 1, this does not appear to be significant. Yellow ochre was rarely used.

The organic reds on these paintings need more precise identification before any significance can be attached to the variations in their occurrence. The presence of an organic brown color on one-third of the paintings from the mid-17th to mid-18th century is of considerable interest; this pigment also needs further identification.

The copper greens must also be more precisely characterized before conclusions can be drawn about their use, although it appears that they were substitutes for malachite, especially on later *Ukiyo-e* paintings. One of them, emerald green, first manufactured in 1814, would only be expected on late *Ukiyo-e* paintings.

Prussian blue is the other pigment of this series with a definite first date of manufacture, in Europe in 1704. One would not expect it to be in use in Japan before the early 18th century, and it is interesting that Prussian blue reached Japan as early as it did; the three paintings in Group 2 on which it is found date early in the 18th century. Indigo was not common on the earliest paintings, and its use may have declined somewhat towards the end of the period. This might reflect its replacement by Prussian blue, but this decline may also be only an indication of the limits to sampling methods discussed above.

The less widely used pigments fall into various categories. The four occurrences each of lead white and ultramarine appear to be special isolated instances. Possibly the most interesting pigments, both because of the variation in their occurrence at different dates and because they occur at all, are orpiment and smalt. Orpiment is rare on these paintings and its use here is curious, as it is not in the tradition of Japanese pigments. It has not been found to date on any other Japanese paintings in the Freer collection, nor has it yet been reported on Chinese paintings, with the exception of the 10th–11th century paintings from Tun-huang. Smalt is used on these *Ukiyo-e* paintings at all dates, being most common from the mid-17th to the end of the 18th century. Again, this is not a traditional pigment in Japan, having been used there only since the 16th century, and then only occasionally. Only two other occurrences of smalt have been found on 16th and 17th century paintings, not of the *Ukiyo-e* school, in the Freer. It is not found on Chinese paintings, except for some occurrences on wall paintings dating as early as the 11th century.[27]

In the main, these *Ukiyo-e* artists used traditional pigments. The apparent exceptions, orpiment and smalt in particular, are of interest. Identification of pigments from additional paintings, further study of some of the unusual copper green and brown pigments, and more study of the organic reds, may throw more light on these exceptions to what has been accepted as the Japanese tradition.

ACKNOWLEDGMENTS

The original impetus for this study was provided by Rutherford J. Gettens, and pigment identifications on 48 of the paintings under discussion were made by him. Harold P. Stern, an authority on *Ukiyo-e* painting and Director of the Freer Gallery from 1970 until his death in 1977, provided much encouragement. Richard FitzHugh developed the program for tabulating the data on pigment occurrences. Kazuo Yamasaki made a number of helpful comments on an early draft of this paper, particularly in connection with Japanese pigment names.

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[27] Mühlethaler and Thissen, "Smalt."

URUSHI AND CONSERVATION: THE USE OF JAPANESE LACQUER IN THE RESTORATION OF JAPANESE ART

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INTRODUCTION

". . . Art works in lacquer are the most perfect objects which ever issued from the hands of man."[1] This statement, written in 1886, expressed the sentiment of Western art collectors who were beginning to acquire Japanese works as a result of the opening of Japan to the West in the latter half of the nineteenth century. Lacquer objects presented not only a whole new aesthetic experience but an entirely new kind of material as well, unrivalled by anything available in the Western world. Since then, generations of collectors have continued to be fascinated by Japanese lacquer, known as *urushi*.

Urushi is a fascinating material for reasons beyond its use in making highly decorative Japanese lacquer objects. It is also one of the oldest and most versatile conservation materials and is still in use at the present time. Few materials in conservation can lay claim to the versatility of *urushi* which serves so many functions by the addition of a few materials. While there are a number of excellent recently published texts in English that discuss the history and techniques employed by lacquer artists in Japan,[2] there is virtually nothing available in any Western language which documents *urushi* as a conservation material. This article will attempt to fill this gap and add a chapter to the history of conservation as well as to the history of *urushi*.

URUSHI: GENERAL BACKGROUND

Urushi is a highly viscous natural latex which comes from the sap of the lacquer tree, *Rhus vernicifera*. Like a number of other trees in the *Rhus* family such as *Rhus toxicodendron* (poison ivy), *Rhus vernicifera* gives a sap which causes extreme skin irritation. While the sap can be used directly as raw *urushi*, usually it is refined by the manufacturer before it is sold

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[1] Louis Gonse, *L'art Japonais*, (Paris: Maison Quanin, 1886), p. 245.

[2] Some recently published books oriented to technique are: K. Herberts, *Oriental Lacquer, Art and Technique* (New York: Harry N. Abrams, Inc., 1963); Melvin and Betty Jahss, *Inro and Other Miniature Forms of Japanese Lacquer Art* (Rutland, Vermont: Charles E. Tuttle Company, 1971); Beatrix von Ragué, *A History of Japanese Lacquerwork* (Toronto: University of Toronto Press, 1976); Tomio Yoshino, *Japanese Lacquer Ware* (Tokyo: Tourist Library, 1959), vol. 25.

to the artist. Refining may vary with each dealer and is considered to be proprietary; it involves mixing different kinds of lacquers, stirring the lacquer in large vats, exposing it to sun or heat and straining it to remove impurities. Differences in refining technique and in the quality of the unprocessed *urushi* account for the variety of *urushi* resins available for use.[3]

Few natural resins can equal *urushi* in terms of its hardness, resistance to water damage, general weatherability, and high frictional resistance. Objects coated with *urushi* can be used, with proper care, as items for everyday use and still survive in an excellent state of preservation for many years.

One of the earliest historical uses of lacquer in Japan was to preserve, protect, and harden a substrate. An excavated late Jomon period (ca. 1000–250 B.C.) basket was constructed of sliced and woven fibers and covered with a thick coating of red lacquer.[4] The lacquer acted as an adhesive which held the fibers together, provided rigidity, and served as a waterproof surface coating. In more recent times, sword blades which could not be properly maintained were coated with *urushi* to protect the blade. Although the *urushi* will eventually darken and obscure the blade, an experienced sword polisher, using the abrasives of his trade, could remove the *urushi*. Even more recently, Japanese soldiers in World War II sometimes coated the metallic parts of their weapons with *urushi* for the dual purpose of protecting the weapon from rust and reducing reflection.

The adhesive property of *urushi* is often used as a theme in stories which relate the discovery of *urushi*. In one such story, people were baffled by the heavy beehives which hung tenaciously to their tree branches through all kinds of weather. They watched the bees gather the sap of a particular tree and use it as an adhesive for their hives, and they thus discovered *urushi*.

An interesting illustration of the durability of *urushi* took place in the last century. In 1873, the Japanese submitted a number of gold lacquer wares to the International Exposition at Vienna in order to introduce the Western world to the crafts of Japan. While the objects were being transported back to Japan, the French mail steam ship "Nile" was wrecked off the coast of Izu in February, 1874. Over a year later, on July 18, 1875, a gold lacquered book shelf and book stand were recovered and found to be in excellent condition. Ironically, the Japanese, who sent these objects in order to impress the Western world, were in turn so impressed by the durability of their own lacquer that the pieces were subsequently put on display at the Tokyo Imperial Museum as a testament to the permanence and superior quality of Japanese lacquer.[5]

The durable, protective and adhesive qualities of *urushi* are based on its unusual chemical properties. *Urushi* is composed of several different materials. Urushiol, the prime constituent of *urushi*, is a combination of four components which have the structure of a catechol (a benzene ring with two adjacent hydroxyl groups) with a 15 carbon side chain. The differences among the four components are in the degree of saturation of the side chains. The presence of the enzyme laccase and carbohydrates in *urushi* serve to catalyze and accelerate the cross-linking of the various urushiol components. A high humidity and a restricted temperature range are necessary for the efficient catalytic function of these materials. Because there are from one to three sites available for linkage between the urushiol components, a densely cross-linked polymerization reaction takes place.[6]

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[3] A good description of the preparation of *urushi* is given by J. J. Quinn, "The Lacquer Industry of Japan," *Transactions of the Asiatic Society of Japan*, vol. 9 (1881), pp. 1–30.

[4] J. Edward Kidder, *Japan Before Buddhism* (New York: Frederick A. Praeger, 1966, revised), p. 62.

[5] Noritake Tsuda, Japanese Lacquer, (unpublished manuscript in the Metropolitan Museum of Art, 1908–12), section on Gold Lacquer in the Tokugawa Era, p. 7.

The polymerized *urushi* film is far more closely related to the structure of some modern thermosetting plastic resins, e.g. bakelite and melamine, than to the type of film obtained with natural resins. This structural similarity to modern resins suggests analogous physical properties such as solvent resistance, strength and durability. *Urushi* differs from such natural products as drying oils in that the latter harden mainly by auto-oxidation where the cross-links consist mainly of oxygen-oxygen or peroxide bonds. Such linkages are not as extensive or stable as those in the drying of *urushi*. The unique properties of *urushi* led Joseph Needham to observe that *urushi* is "the most ancient industrial plastic known to man."[7]

URUSHI IN THE CONSERVATION OF LACQUER OBJECTS

There is a direct relationship between the quality of a lacquer work and its degree of preservation. A lacquer object prepared according to the most traditional and demanding techniques, using the highest quality materials, will tend to survive much better in adverse conditions than ones of lesser quality and craftsmanship. High quality lacquers offer better protection to the structural substrate; they have harder surfaces, better interlayer bonding and less permeability to moisture attack, and the most beautiful finish.

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[6] For a fuller account of the chemistry of *urushi*, the following articles, listed chronologically, can be consulted, especially the works of Dawson, Nakamura and Kato and Kumanotani. S. Hiraga, unpublished manuscript essay, 1877, in the Library of Tokyo University, referred to by Korschelt and Yoshida (see below) as the first account of the chemistry of Japanese lacquer; O. Korschelt and H. Yoshida, "The Chemistry of Japanese Lacquer," *Transactions of the Asiatic Society of Japan*, vol. 12 (1885), pp. 182–220; Riko Majima, *Untersuchungen über den Japanlack*, (Tokyo: Iwata Institute of Plant Chemistry, 1924), vol. 1. This volume contains his collected work on Japanese lacquer. G. A. Hill, V. Mattacotti and W. D. Graham, "The Toxic Principle of Poison Ivy," *Journal of the American Chemical Society*, vol. 56 (1934), pp. 2736–2738; William Symes and Charles Dawson, "Poison Ivy 'Urushiol'," *Journal of the American Chemical Society*, vol. 76 (1954), pp. 2959–2963. S. V. Sunthankar and Charles Dawson, "The Structural Identification of the Olefinic Components of Japanese Lac Urushiol," *Journal of the American Chemical Society*, vol. 76 (1954) pp. 5070–5074; Takao Nakamura, "Purification and Physico Chemical Properties of Laccase," *Biochimica et Biophysica Acta*, vol. 30 (1958), pp. 538–542; Takao Nakamura, "On the Mechanism of the Reaction of the Reduced Laccase with Oxygen," *Biochimica et Biophysica Acta*, vol. 42 (1960), pp. 499–505; Ju Kumanotani, Takashi Kato and Aizo Hikosaka, "Studies on Japanese Lacquer: Urushiol Dimerization by the Coupling Reaction Between Urushiol Quinone and a Triolefinic Component of Urushiol," *Journal of Polymer Science*, Part A-1, vol. 7 (1969) pp. 1455–1465; Ju Kumanotani, Takashi Kato and Aizo Hikosaka, "Studies on Japanese Lacquer: Film Formation via o-Quinone and Enzymic Oxidation of Urushiol Homologues Catalyzed by Laccase," *Journal of Polymer Science*, Part C, no. 23 (1968), pp. 519–531; Takashi Kato and Ju Kumanotani, "Studies on the Film Formation Mechanism of Naturally Occurring Polyphenolic Coating Materials: The Role of Dehydrogenative Coupling Reaction with o-Quinones," *International Symposium on Macromolecular Chemistry*, Budapest, vol. 5 (1969), pp. 105–108.

[7] Ts'ao T'ien Ch'in, Ho Ping-Yö and Joseph Needham, "An Early Medieval Chinese Alchemical Text," *Ambix* (London), vol. 7, no. 3 (1959), p. 152.

The traditional techniques employed in conserving lacquer objects are similar to the procedures used in making the original piece. The conservation of wood statuary and ceramics, where *urushi* is used as the conservation material, is also based on an understanding of these basic procedures of the lacquer artist.

In creating a lacquer object, the layers of *urushi* are applied to specially prepared base materials[8] in successive steps. As each layer is applied, it is dried for three or four days in a special "wet box" which provides the high level of humidity necessary for hardening the lacquer, and then polished. This procedure must be repeated for each layer. A typical *roiro* finish involves the following steps:

(1) The ground layer: A piece of silk or hemp cloth, impregnated with *nori urushi* (a mixture of *urushi* and rice flour), is applied on the surface of the base material. Coarse *jinoko* (pulverized powder from unglazed earthenware) mixed with *urushi* is applied over the cloth, dried and sanded with a whetstone. This step is repeated using finer grades of *jinoko* with each application. Finally, a mixture of *tonoko* (a special clay powder which is finer than *jinoko*) and *urushi* is substituted for *jinoko*. This step is also repeated using finer grades of *tonoko* until a smooth, even layer is produced.

(2) The basic and intermediate foundation coating (*shitanuri* and *nakanuri*): An urushi blackened by iron powder that has been steeped in vinegar is applied, dried and polished with magnolia charcoal. This step is repeated. If a gold dust background is to be applied, as in the *nashiji* technique (where a transparent *urushi* called *nashiji urushi* completely covers the metallic ground), it is applied at the conclusion of this stage and the *uwanuri* step is omitted.

(3) The final surface coating (*uwanuri*): *roiro urushi*, a lacquer of the very highest quality which has been blackened by iron, is applied, dried and polished with magnolia charcoal. This step is repeated until eventually finer camellia wood charcoal is substituted for magnolia charcoal.

(4) The polish (*suri urushi*): The *urushi* is rubbed into the surface with cotton, and the excess is wiped off. After drying, it is finger polished with *tonoko* and oil. The step is repeated at least three more times, using *tonoko* and *tsunoko* (calcined deer's horn ash) in oil, then *tsunoko* in oil and finally *tsunoko* alone. In the final step, raw *urushi* diluted with water is rubbed on the surface. The excess *urushi* is rubbed off with rice paper which has been softened by crumpling it. After the *urushi* has dried for a few hours, it is polished with a dab of oil on the fingers until the surface develops a deep black finish.

The most commonly applied type of design employs a *makie* ("sprinkled picture") technique where the design is painted in lacquer with a brush on the prepared lacquer surface. Before it dries, gold, silver, metallic, or colored powder is dusted on. The three major *makie* techniques discussed in order of their historical development are *togidashi*, *hiramakie*, and *takamakie*.

(1) *Togidashi* (embedded burnished design): The design is applied as briefly described above in the *makie* technique. The entire surface is coated with several layers of urushi which are dried and polished with

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[8] Often elaborate preparations are involved in preparing a wooden base for the *roiro* surface. Channels are cut into the wood and filled with *urushi* in order to minimize damage from expansion and contraction. Also, the wood should have equal thicknesses of *urushi* on both sides to prevent warpage.

hinoki (cypress) charcoal until the pattern is revealed. It is then polished with *tsunoko* and oil and a final transparent layer of *urushi* is applied over the entire surface. The result is a highly polished, flat surface.

(2) *Hiramakie* ("flat sprinkled picture")—The design is applied as above. The design only is covered with *urushi* thinned with camphor, dried and polished. This also results in a relatively flat design on the surface of the *urushi*.

(3) *Takamakie* ("raised sprinkled picture"): A design is drawn with *urushi* and sprinkled with charcoal powder to produce a raised relief. The loose powder on top of the design is covered with raw *urushi* to secure it. After the *urushi* dries, the surface is polished with charcoal until it is flat. This process is repeated until the desired height of the relief is attained, then the surface is prepared by applying coats of lacquer and polishing the latter with charcoal after it dries. The same technique is used as for the *hiramakie* finish to cover the raised relief.

Traditionally, a lacquer with a highly polished *roiro* finish requires 33 steps. A design layer applied on the *roiro* layer would require many additional steps. It is clear that lacquers are complicated, multilayered structures[9] where the final appearance is very much affected by the manner in which the surface is built up.

Types of damage to lacquer finishes fall into a number of categories:

(1) Damage as a result of physical abuse, such as when a piece is dropped or severely abraded.

(2) Alterations in surface appearance as a result of the application of waxes, furniture cleaners, chemicals, and accretions of dirt and grease, especially from fingerprints. Most of these problems can be remedied by a careful surface cleaning, in much the same way as the restorer would treat any delicate, moisture-sensitive surface such as ivory. However, some accretions are difficult to remove and can ruin the fine polish on the surface of the piece. In this case, the accretion can be abraded away with *tonoko* and oil and repolished as in step 4 of the *roiro* technique.

(3) Permanent discoloration from bleaching as a result of overexposure to sunlight. This is an irreversible damage.

(4). Tarnishing or corrosion of applied metal parts of the design, such as tarnishing of silver or carbonate formations on lead surfaces. The corrosion or tarnish must be carefully removed by a treatment tailored to the way the metal was applied to the lacquer base and the thickness of the metal. After cleaning, the metal can be protected either with *urushi* or synthetic plastic.

(5) Damage to the surface as a result of movement in the moisture-sensitive base material as it responds to changes in relative humidity. While the *urushi* skin is not sensitive to changes in humidity, the object's substrate, which is usually made from wood, can be very sensitive to such changes. A slight permeability in the lacquer film permits the moisture content of the wood to respond to variations in relative humidity, resulting in movement of the wood substrate. Such movement in the wood can cause cracking and cupping in the inflexible *urushi* skin.

Well made lacquer objects have shown a remarkable ability to withstand the generally high level of humidity in Japan, because the intact *urushi* skin acts as an effective moisture barrier. The large fluctuations in humidity from a maximum in June to the driest period during the winter months seem to have little adverse effect.

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[9] Photo-micrographs of layers in a Chinese lacquer have been published by Sir Harry Garner, "Technical Studies of Oriental Lacquer," *Studies in Conservation*, vol. 8 (1963), pp. 94–95.

However, lacquer which has been exported to countries with a lower *average* relative humidity than Japan are especially prone to damage. The wood, which has been preconditioned to the high relative humidity in Japan, will gradually equilibrate to the lower relative humidity of its new environment. This gradual drying out process causes permanent shrinkage, unlike the situation in Japan where a slight shrinkage during the dry winter months is offset by an equivalent expansion during periods of higher humidity. The widespread use of central heating in winter magnifies the problem by further reducing the relative humidity during those months when the relative humidity is already at its lowest level.

A constant relative humidity of 60% is generally recommended for the storage and exhibition of lacquer objects.[10] This fairly high value reflects the high relative humidity in Japan to which the object was presumably equilibrated. However, if a piece was stored over a long period in a dry environment where the wood base has adjusted to a low humidity, it might be best to store it at a humidity level below the normally recommended 60% R.H. level; a relative humidity approximating the level to which the wood has already adjusted is preferred so as to avoid subsequent expansion or contraction in the wood.

The surface damages which result from the shrinking of the substrate are surface cracks, cleavage and cupping. For treating cracks, the surface is rubbed with *suri urushi* so that it soaks into the cracks and the excess is wiped off. The piece is then repolished with *tonoko* and *tsunoko* as in the *roiro* finish. Cleavage is set down with injections of *urushi* thinned with camphor or an especially thin variety like *kijiro urushi*. It is difficult to know how much *urushi* to apply since too little will be ineffective and too much may cause severe shrinkage and buckling of the surface upon drying. Cupping, where sections of lacquer curl at the edges, is an irreparable damage. It can be treated as cleavage where the raised edges are preserved or it can be sanded down and filled in order to obtain a smooth finish once again.

Pieces that have been damaged and then treated only at the surface, as discussed above, will usually be most susceptible to subsequent damage because the substrate would already have been weakened during the initial damage. Since the restoration only re-adheres loose areas and fills losses, but does not necessarily consolidate internal weaknesses or blind cleavage, damaged pieces are particularly prone to further problems.

The steps for filling losses in lacquer are similar to the initial techniques used to make lacquer finishes and follow the same sequence:

(1) The ground layer: If the loss goes to the depth of the base material or the *urushi* and cloth ground layer, it is filled with *sabi urushi* (*urushi* and *tonoko*) to the original *nakanuri* layer, and is finished as in step (2) below.

(2) The background: If the loss goes into the *nakanuri* layer (the fine, colored layer just above the cloth layer), a layer of *urushi* like the one described in the *nakanuri* (step 2)

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[10] *Expert Meeting on the Care of Works of Art in Loan Exhibitions between the United States and Japan*, Papers from Japan, an unpublished report prepared for a Meeting at the Freer Gallery of Art, July 23, 1975, p. 17.

section of the *roiro* finish is applied, dried, and sanded; several layers may be necessary depending on the extent of the loss. At this point, the background metal powder and *nashiji urushi* is added as needed.

(3) The final surface: As a continuation of step (2) or if the upper *uwanuri* layer is damaged, *roiro urushi* is applied, dried and polished with charcoal. Depending on the nature of the damage, this may be repeated.

(4) The polish: In all cases of surface abrasion or in continuation of the above procedures, the surface is repolished as in step 4 of the *roiro* finish using *suri urushi*.

(5) The design: Any loss in the *makie* design may be redone in the original technique.

According to Japanese restoration philosophy, the ideal restoration from both a functional and a decorative point of view should duplicate the techniques employed in making the original piece, since each layer in the original is usually justified by a functional or decorative purpose. Such a perfect restoration is usually impractical or impossible.

One major difficulty is color matching. *Urushi* gradually undergoes a color shift as it ages and becomes more transparent with time. If a repair is done with *urushi*, the restorer must try to make allowances for a change in his restoration so that upon aging it will approximate the original color. However, it is hard to predict exactly how the *urushi* will change over time. This explains why new restorations, as well as many older restorations, may appear as areas of discoloration on a lacquer piece. An example of such a restoration is a rectangular box of the 12th century (fig. 1), where the restored area of the lower right corner stands out as a light brown patch against a deeper dark brown background. Matching up precious metals is also a problem. Certain kinds of gold powders used in earlier periods are no longer available and analogues are hard to come by.

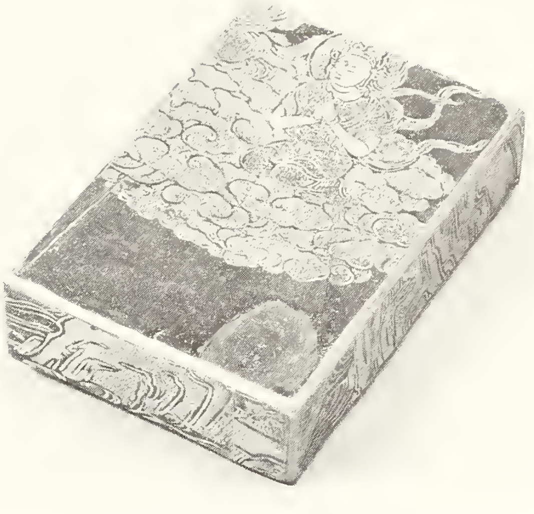

Fig. 1. —Lacquer Box, 12th century, (Courtesy Museum of Fine Arts, Boston, 11.10156).

Another difficulty is achieving an invisible fill. If the layers of *urushi* are applied too thickly, it is hard to get a perfectly flat fill. If the layers are too thinly applied, there is greater risk of damaging the adjacent original areas when each layer is sanded. Original parts, especially areas of raised relief, can be protected by a thin piece of metal foil during sanding. To avoid concavities, the loss must be filled with a succession of thin applications of *urushi*, each of which is carefully sanded so as to avoid any ridges at the edges or depressions in the center. The ability to get a perfectly smooth fill is further complicated if background gold such as is used in the *nashiji* layer is applied. The restorer must know exactly at what underlayer of the fill to apply the gold since only a few layers can be

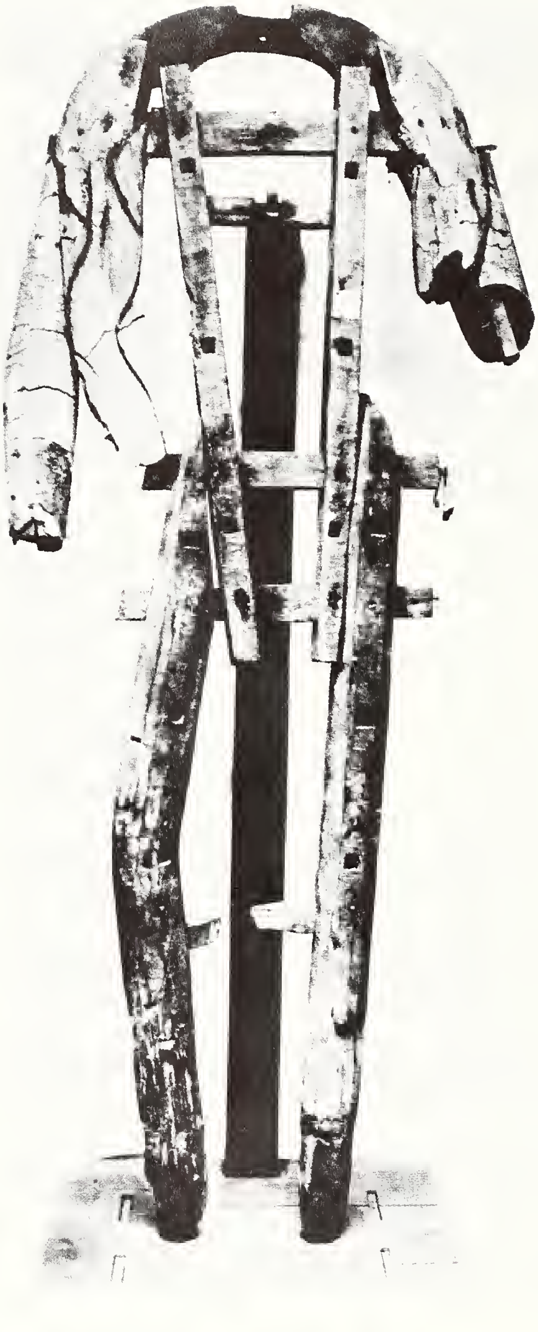

FIG. 2.—Armature for a hollow lacquer figure, 8th century, Akishino Temple, Nara.

applied over the gold to give the proper appearance; otherwise he must underfill or overfill the loss.

The steps involved in doing a superior repair are numerous and time-consuming. Good materials and a high level of skill are the essence of excellent lacquer work as well as high quality lacquer restoration.

URUSHI AND SCULPTURE

During the later Nara period (710–784 A.D.), dry lacquer replaced bronze as the dominant medium for Japanese Buddhist sculpture. Dry lacquer, called *kanshitsu*, consists of many layers of cloth impregnated and covered with *urushi*, which are built up over a wooden armature (fig. 2). In the *dasshin kanshitsu* technique, the cloth and *urushi* are built up on a clay base and wooden armature; after drying, the core of clay and wood is removed. The surface of a dry lacquer sculpture is covered with *sabi urushi* and finished with gold and color. The *kanshitsu* technique has a permanence which crumbling clay, corroding bronze, or shrinking wood cannot match. However, constructing a dry lacquer piece is time-consuming and uses great quantities of *urushi*.

By the early Heian period (784–897 A.D.), the temporary clay and wooden armature of the dry lacquer technique was replaced by a solid wooden core which could be precisely carved and simply finished with a thin coat of *urushi*. Both the amount of *urushi* used and the time involved were thereby reduced. Early sculptures of this type were carved from a single block of wood according to the *ichiboku zukuri* (single block construction) technique. In a variation called the *yosegi shiki ichiboku zukuri* technique (single block with multiple sections added on), separate limbs were carved and added on to the body. In order to reduce the weight and chances of cracking, the wood was hollowed out from the back and a new back was attached. By the latter part of the Heian period (eleventh century), sculptors shifted to yet another technique, *yosegi zukuri* (multiple sections). The figure was built up from many smaller individually carved parts, which were joined together with metal nails or staples and an animal glue. *Urushi* mixed with sawdust was used only to cover the seams of the joins and as a decorative surface coating (figs. 3, 4, 5, 6, 7).

Sculpture done in the *yosegi zukuri* technique generally requires restoration work within 200 years. The glue joins gradually weaken because of the contraction and expansion of the wood as it responds to cyclical changes in humidity. Older restorations usually duplicated the original technique used to make the statue, i.e., animal glue was used as the adhesive, and *urushi* only served a decorative function.

During the Meiji era (1868–1912), there was a revival of interest in the ancient history of Japan. At that time Kakuzo Okakura, best known in the West for his *The Book of Tea*, noticed the well preserved state of many Nara period dry lacquer sculptures. These observations led him to suggest the substitution of *urushi* for glue in the restoration of wooden sculpture to give a more permanent join. His idea was applied intermittently through the Meiji era, became widely used in the Taisho era (1912–1926) and is now common practice among Japanese conservators of all types of wooden sculpture.

Today *urushi* has four functions in the conservation of wood and dry lacquer sculpture: (1) as an adhesive, (2) as a fill and consolidative material, (3) as a material for replacing fine carving or relief design; and (4) as a surface coating.

In the case of dry lacquer, structural damages often require the application of fresh gauze material and lacquer, to be applied and built up in layers just as in the original piece. Cleaved layers of cloth are reattached with *mugi urushi* (*urushi* mixed with flour) as the adhesive. Where losses occur in the upper layer of the original skin, *sabi urushi* (*urushi* mixed with clay powder) similar in composition to the original skin, is used for the fill. Fine sculptural details such as parts of the face may be built up with *kokuso urushi* (*urushi* mixed with flour and sawdust), and carved in imitation of the original, followed by *sabi urushi* and *kuro urushi* (black *urushi*), and finished with gold or pigment as necessary.

Solid wood sculpture is restored in a similar way.[11] Sections and appendages are reattached with metal nails or staples and *mugi urushi*. Wormholes and splits are filled with *kokuso urushi* with a typical consistency of two parts *mugi urushi* and three parts sawdust. The replacement of fine sculptural details such as eyebrows is also done with *kokuso urushi*. *Kokuso urushi* is also used in conjunction with *mugi urushi* to join major structural sections (such as arms and body); the *mugi urushi* fills the seams of the joins. In the event that greater tack is required in the *kokuso urushi*, the amount of sawdust is reduced. The rough *urushi* fills are sanded

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[11] A study of the conservation of wooden statues in Japan was published by Kōchō Nishimura, Toshio Honma and others, "A Traditional Japanese Lacquer Method for Repairing Wooden Buddhist Statues," *The Conservation of Wooden Objects* (London: The International Institute for Conservation of Historic and Artistic Works, 1970), pp. 87–96.

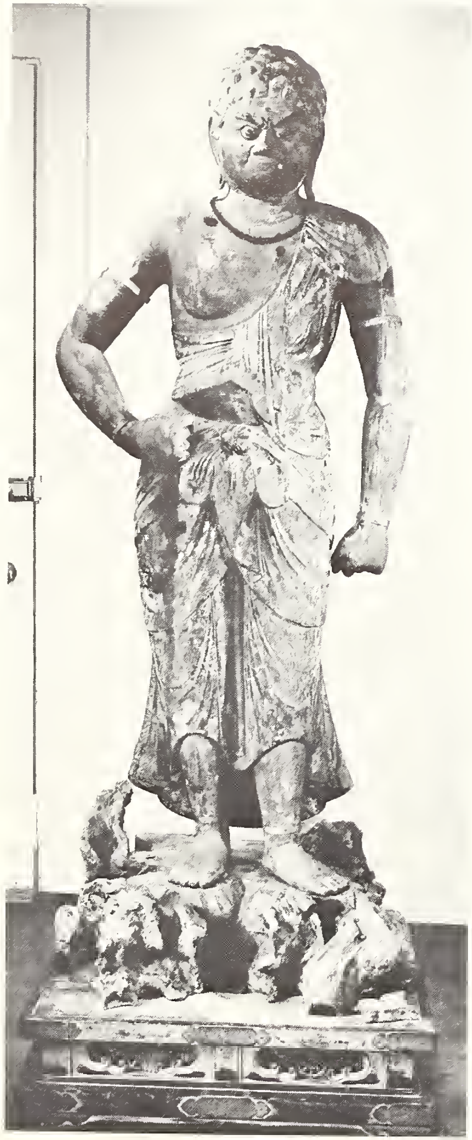

Fig. 3.—Fudo-Myo-o, 12th century, Metropolitan Museum of Art (1972. 268.163), *yosegi zukuri* technique; front.

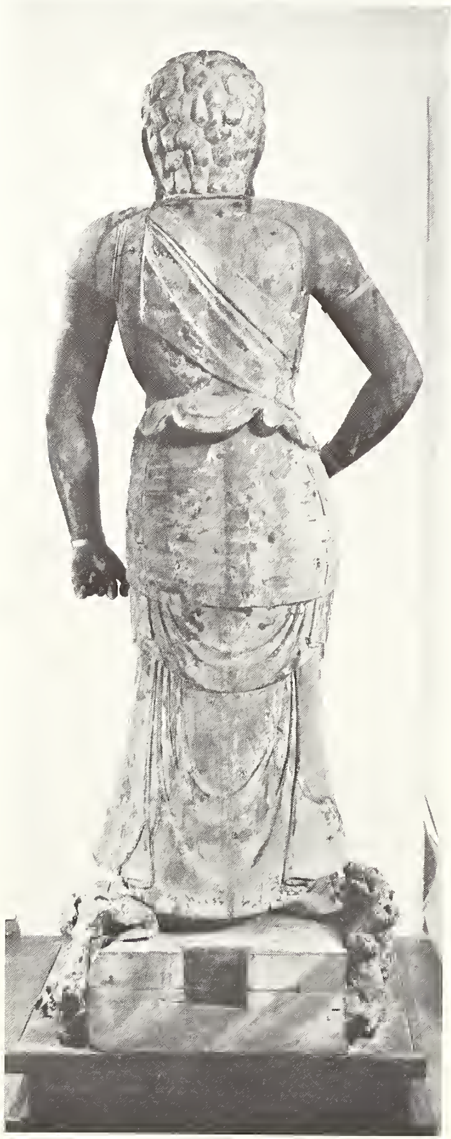

Fig. 4.—Fudo-Myo-o, back.

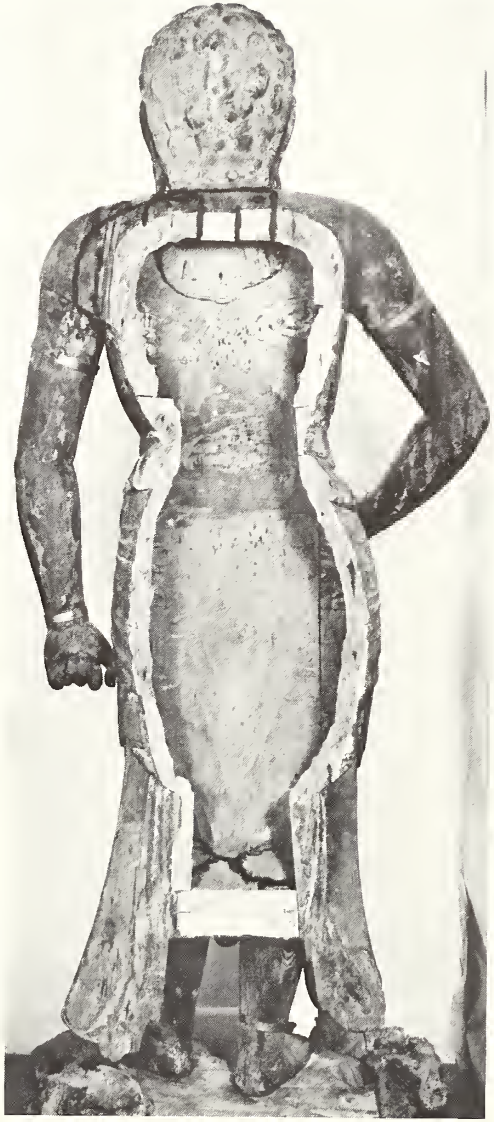

Fig. 5.—Fudo-Myo-o, back removed.

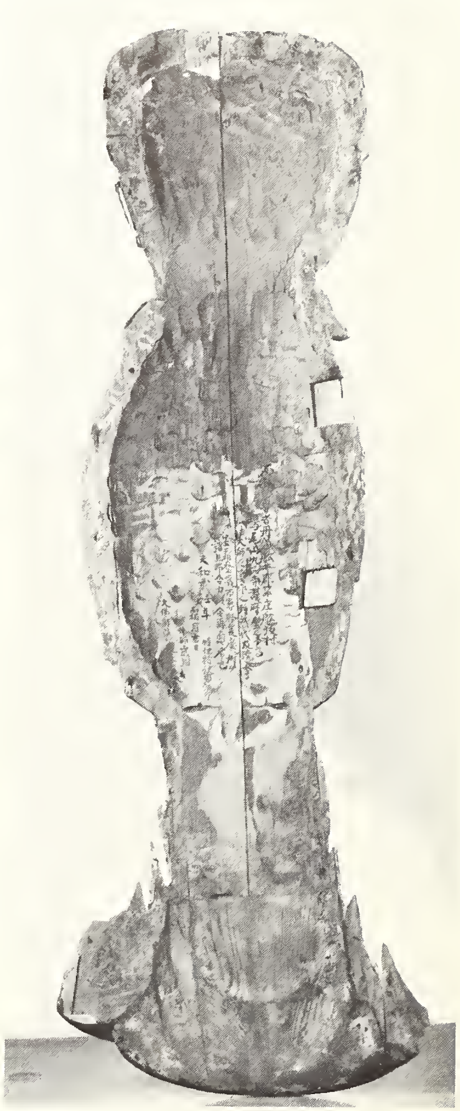

Fig. 6.—Fudo-Myo-o, back inset section. The inscription refers to a previous restoration which was completed "on a good day in November 1682."

down and then covered with *sabi urushi* which in its turn is sanded to a smooth finish. The area is gilded or patinated with colors applied in an animal or seaweed glue. Throughout the process, as each individual layer of *urushi* is applied, it is dried in high humidity and sanded in preparation for the next application. Figure 8–17 illustrate techniques of sculpture restoration using *urushi*, as carried out by Kanya Tsujimoto.

As in the restoration of lacquer objects, the techniques of the restorer of wooden sculpture and dry lacquer are inseparable from those of the original artist. The type and degree of restoration is based on the condition of the object, the ability of the restorer, the knowledge with which to reconstruct losses, and the individual requirements of owner, curator, or temple. Finally, the extent of restoration is governed by the fact that in Japan, many of the finest sculptures can still be appreciated in temple settings. Therefore, the complete replacement of the missing parts is necessary for the sculpture to serve its proper 'function' in its temple setting, as evidence that Buddhist sculpture is still part of Japan's living tradition.

URUSHI AND ARCHITECTURE

Urushi has also played an important role in the history of architecture in Japan. Undoubtedly, during the Nara period when lacquer was used on a large scale for temple architecture, it was appreciated both as a protective and decorative coating. Since *urushi* is a good moisture barrier, it would, if properly applied, protect the wood against water damage and the problems of humidity.

Unfortunately, *urushi* was not always applied in a manner that would best preserve the substrate. Particularly in the case of wooden support columns for buildings where the base of the column is buried underground, an exterior lacquer coat could do more harm than good. If the buried part was not properly sealed, moisture from ground water was wicked up through the column. The *urushi* seal on the surface of the column prevented evaporation of the water, causing the interior of the column to rot.

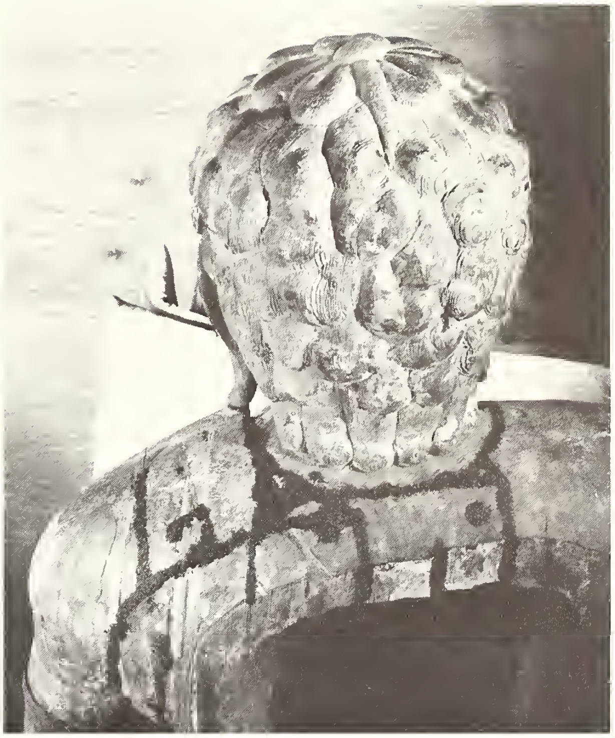

FIG. 7.—Fudo-Myo-o, cracks and losses filled with *kokuso urushi*.

Problems of conserving architectural lacquer are similar to restoring architecture elsewhere in the world. Architectural ornament does not require as delicate a technique as 'fine art' material which is intended to be viewed close-up. Just as the original surface would not have been built up as carefully as in a small *makie* piece, here the loss usually is filled with only a few applications of *urushi*.

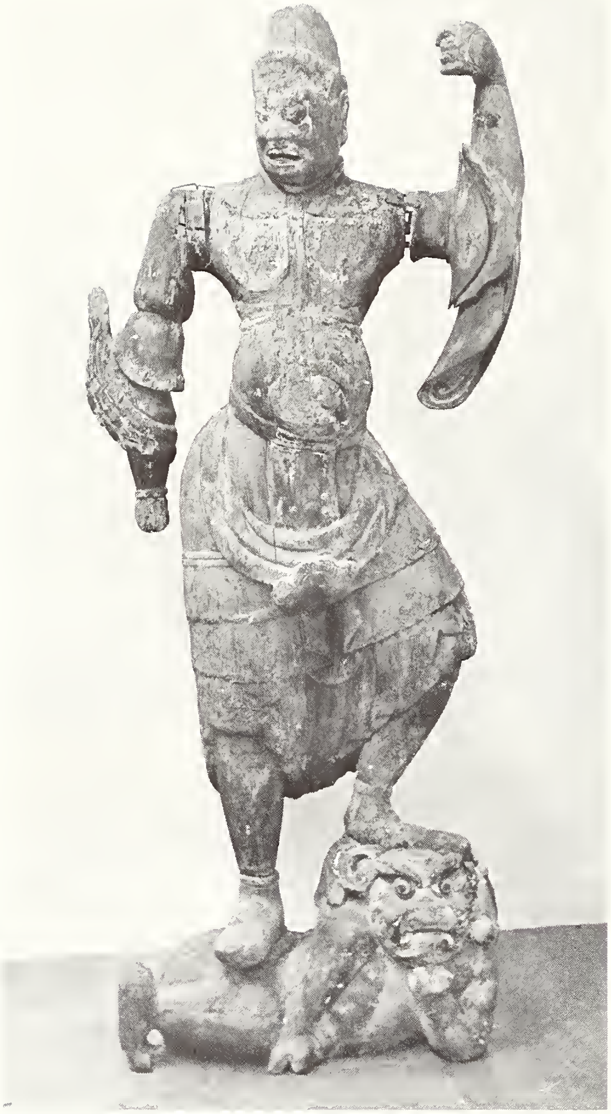

FIG. 8.—*Zochoten* (*Agyo*), guardian figure, 10th–12th century, Metropolitan Museum of Art (17.168.2). The surface of the statue, especially the face, is pulverizing due to the low relative humidity in the United States.

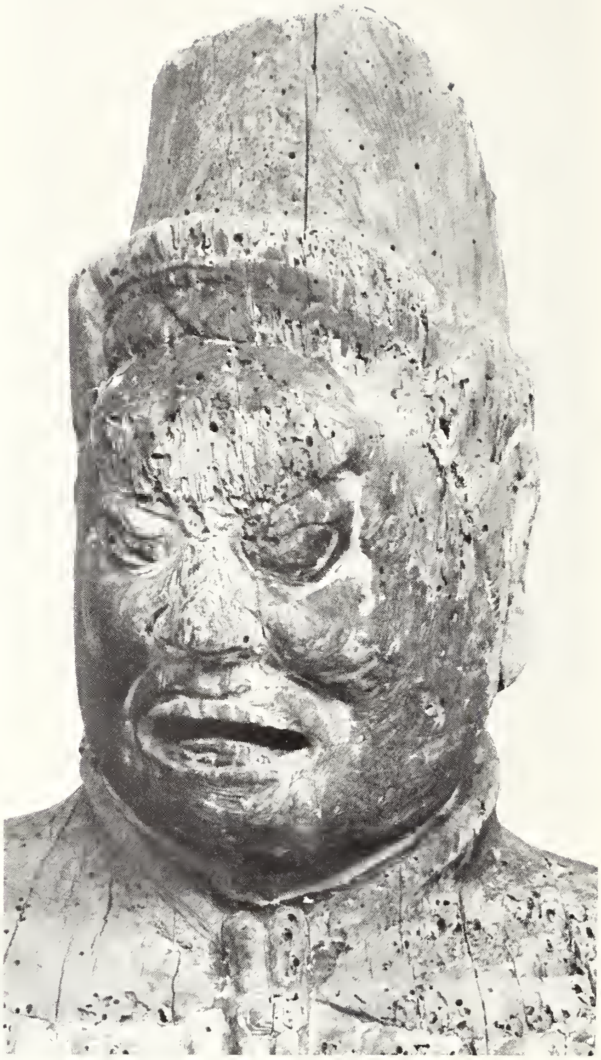

FIG. 9.—*Zochoten*, detail of face, showing old restorations.

Worm holes and cracks may be filled with *kokuso urushi*, and cleavage and cupping may be treated as in the *makie* technique.[12]

At present, plastic resins are displacing *urushi* in architectural restoration. This is based on the ease and speed of application and on the reduced cost of synthetic resins as compared to *urushi*. However, *urushi* continues to have a unique role in the restoration and reconstruction of ancient structures, just

[12] Toshikatsu Nakasato, "Restoration of Lacquered Members of Golden Hall, Chūsonji," *Science for Conservation*, vol. 11 (1973) pp. 29–45, and vol. 13 (1974) pp. 49–74, in Japanese with English summary.

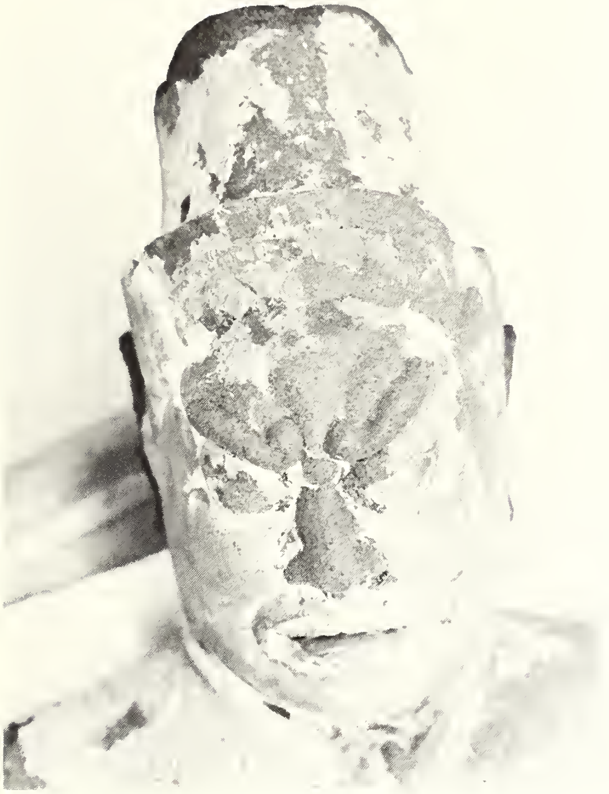

Fig. 10.—*Zochoten*, detail. During restoration, wormholes and splits are filled and details of the face are built up with *kokuso urushi*, which is then carved and sanded to shape.

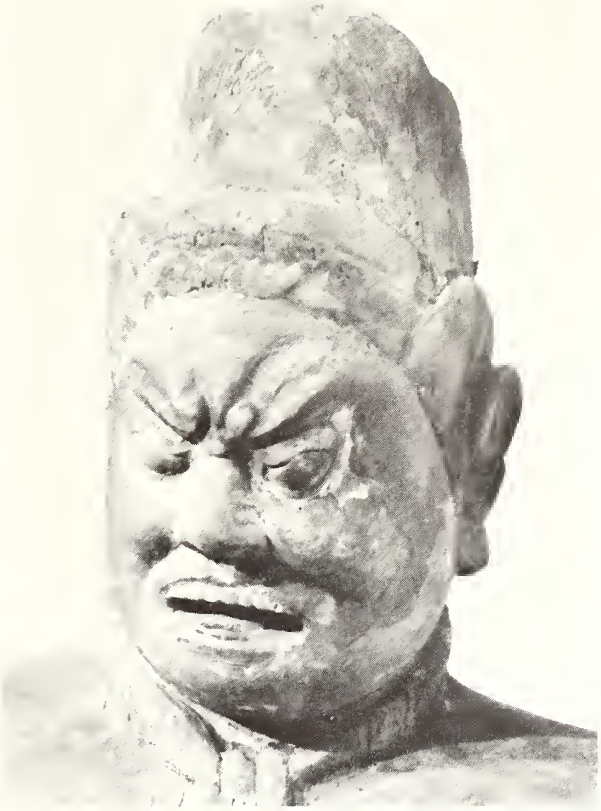

Fig. 11.—*Zochoten*, detail, after restoration. The *kokuso urushi* fills are covered with *sabi urushi* and patinated with pigments in a glue binder.

as the ancient Japanese building crafts and wood-working skills do; in this regard, *urushi* can still hold its own against modern technology.

URUSHI AND CERAMICS

Perhaps the most unusual application of *urushi* in conservation is in the repair of ceramics. In any collection of fine Japanese ceramics, there are pieces which have restorations covered with gold. Unlike ceramic repairs in the West, these restorations are designed to be visible. The willingness of Japanese collectors to accept this kind of repair is part of an overall sensibility with which the Japanese approach ceramics. Jo Okada explained that the Japanese sense of beauty "is so extremely delicate that it seeks a shade of imperfection within perfection. It praises the shadow caused by the light rather than the light itself."[13] Beauty does not mean perfection and a damaged ceramic need not lose the essence of its beauty. This attitude can be understood as

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[13] Jo Okada, "History of Glass in Japan," *Ikebana International* (Tokyo), no. 49 (June 1977) p. 34.

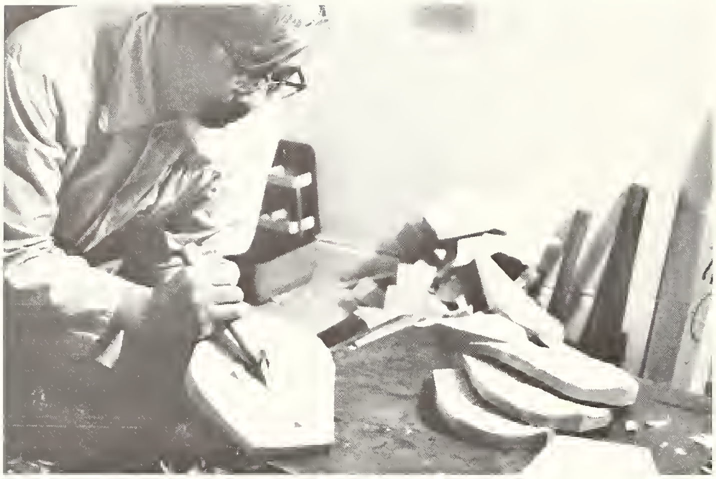


Fig. 12.—Making a lotus base for an Amida Buddha, Metropolitan Museum of Art (26.118). Kanya Tsujimoto carves new petals.

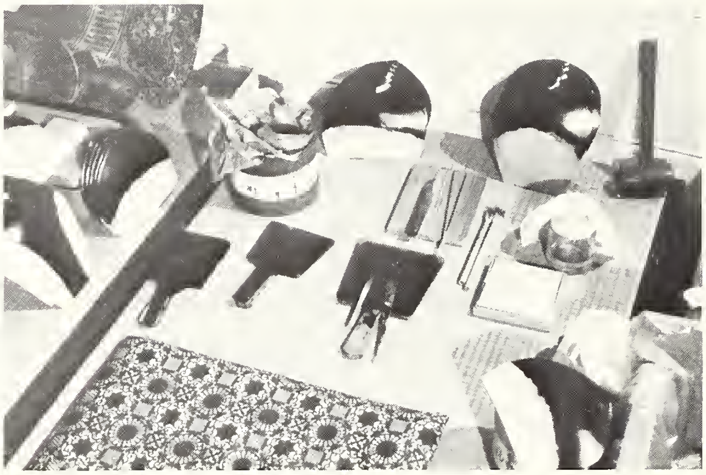


Fig. 13.—The surfaces to be exposed are coated with *kuro urushi* and allowed to dry.

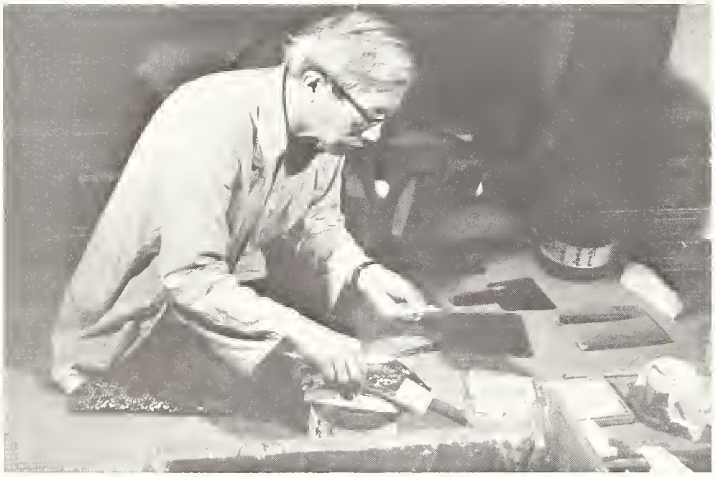


Fig. 14.—Just before the gold leaf is applied, a fresh layer of raw *urushi* is painted on, and the excess wiped off. Gold leaf is applied to the tacky surface.

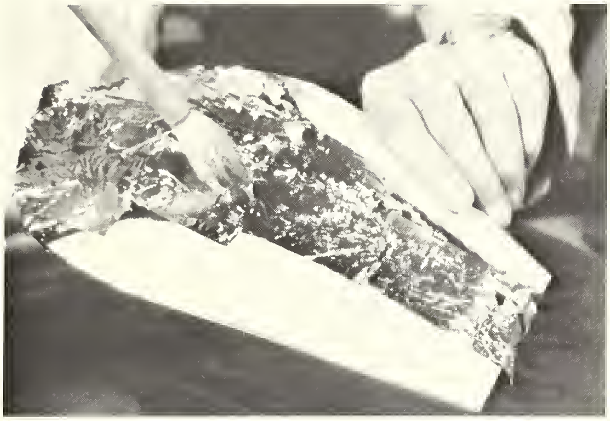


Fig. 15.—The gold is brushed down to a relatively smooth surface.

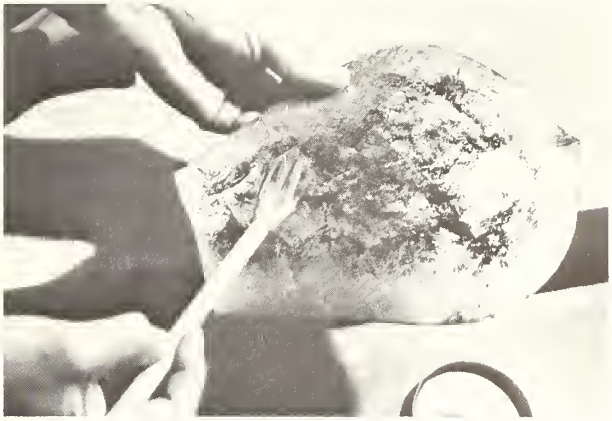


Fig. 16.—Gold is brushed away to imitate wear.

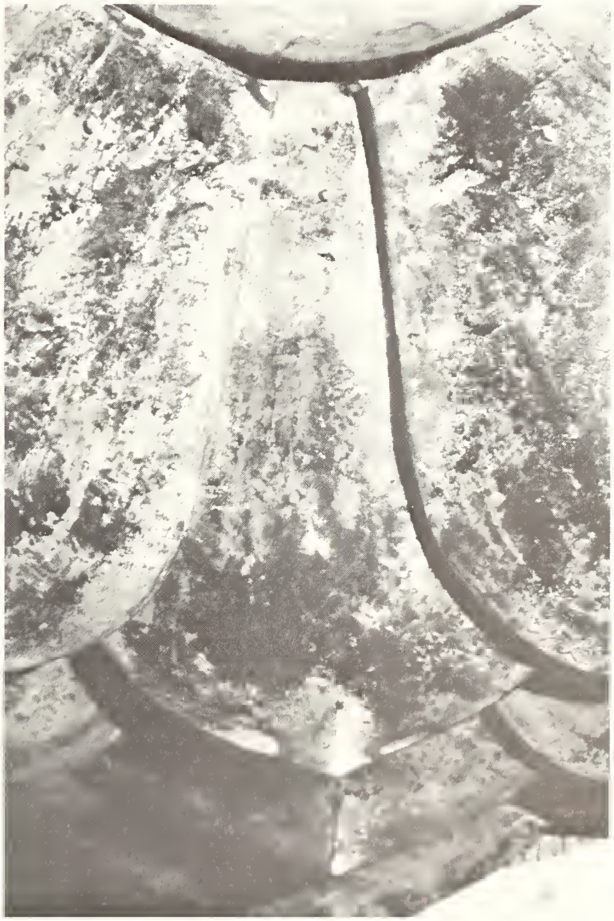


Fig. 17.—The gold is patinated with pigments in a glue binder to suggest an aged surface. The petals are attached to the base with nails.

part of a larger aesthetic sensibility, embodied in such teachings as Zen Buddhism. The beauty of a piece should transcend any incidental damage.

The aesthetic of imperfection seems to apply solely to ceramics and their restoration but does not apply to sculpture, architecture or lacquer wares. Sculpture is meant to be representational, architecture is intended to be functional and lacquer wares are admired for the perfection of their surface. In each of these cases, damage and a visible restoration will detract from the 'purpose' of the object.

The application of *urushi* and gold to the repair of ceramics seems to be a strictly Japanese tradition; such a repair on a Chinese or Korean ceramic would suggest that it once passed through Japanese hands. No date can be assigned to the initial use of *urushi* as an adhesive for ceramics, or for the use of gold in conjunction with *urushi*. It is possible that the combination of *urushi* and gold in ceramic restoration came about under the influence of the aesthetic values of the tea ceremony, and especially may have benefitted from the elaborate decorative tastes of the Momoyama period (1573–1615).

In ceramic restoration *urushi* is used both as an adhesive and as a fill material. As an adhesive, it was unrivalled for strength and durability until the introduction of synthetic adhesives in the twentieth century. It was also a useful alternative to the metal staples used in China and the West for centuries. To join broken sections, a mixture of *urushi* and rice paste or flour is thinly applied to the broken edges, the sections are joined, and the *urushi* hardened in high humidity. Once all the pieces are joined, the line along the break is coated with a thin *urushi* and dusted with gold as in the *hiramakie* technique. The result is the prominent gold line which appears on so many ceramics restored in Japan.

If a slight nick or loss needs restoration, it is first filled to a level just below the surface with *sabi urushi*, dried and sanded to achieve a proper contour, and appropriately finished. Larger losses or replacement of entire sections such as rims or feet can be done in a manner similar to that used in the *kanshitsu* (dry lacquer) technique. A form is used on one side of the loss as a contour guide and backing for the fill. The loss is built up with layers of cloth impregnated with *urushi* and *sabi urushi*. On this rough framework, the body is built up to just below the desired surface and is given the appropriate lacquer finish. In order to avoid having a large repair fall out, the edges are pretreated with a thin *urushi* so that the thick *sabi urushi* filler can attach itself to a firm, non-porous edge.

Examples of ceramic restorations, drawn from the collection of the Freer Gallery of Art, illustrate a large range of techniques and tastes. One type of repair often seen is a filling for fine cracks which developed during the firing of the ceramic. A *raku* tea bowl of the 19th century (fig. 18) displays a line of *urushi* and powdered gold over a fine crack. This gold line stands out like a lightning bolt against the white and pink glaze, giving the ceramic a unique character beyond the intention of the potter. Another *raku* tea bowl of the Edo period (fig. 19) is an example of a simple *urushi* fill. The vertical crack was filled with *urushi* and *tonoko* (*sabi urushi*), shaped and finished with black *urushi*. Through wear and time, the color coincidentally turned to a brown tonality similar to the color of the ceramic.

A Korean(?) bottle of the Yi dynasty (figs. 20, 21) shows a repair done with

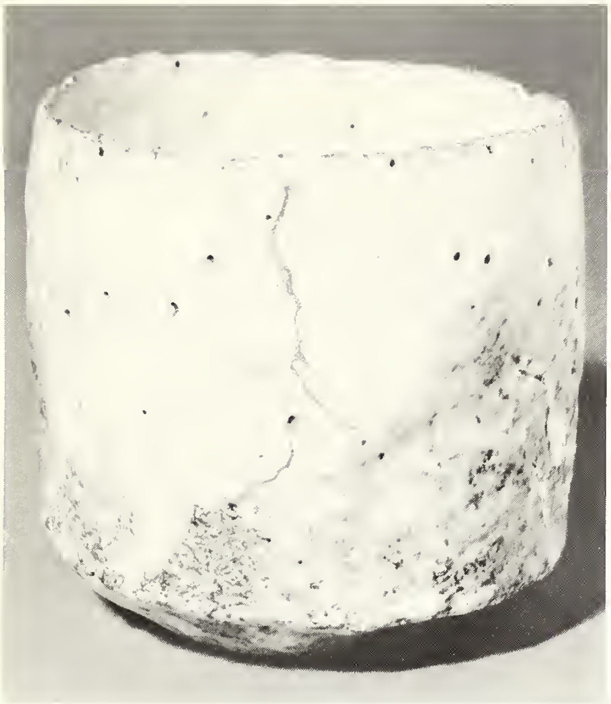


FIG. 18.—Raku tea bowl, Japan, 19th century, Freer Gallery of Art (01.151).

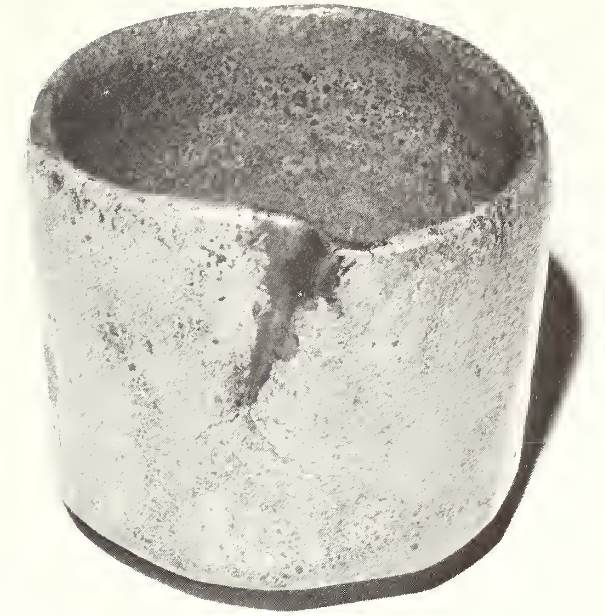


FIG. 19.—Raku tea bowl, Japan, Edo period (1615-1868), Freer Gallery of Art (99.13).

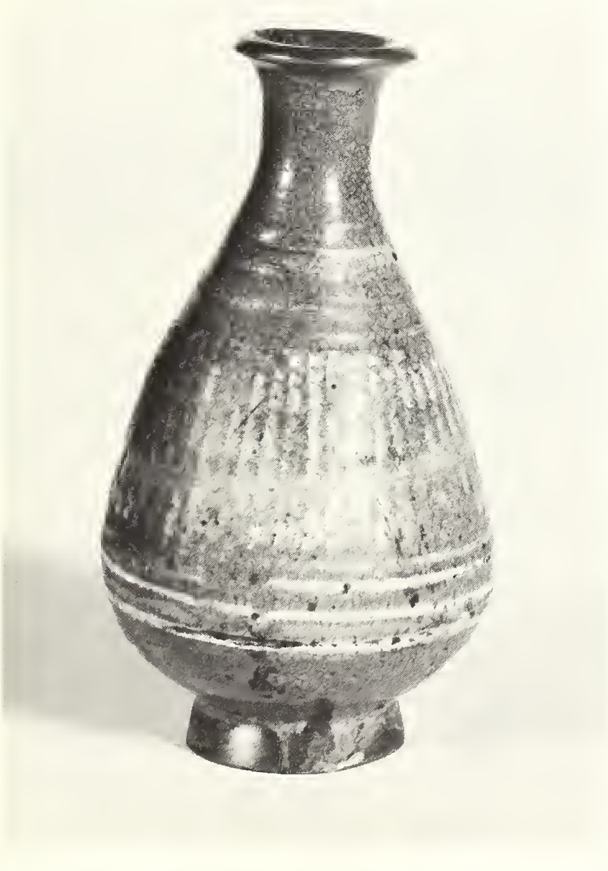


FIG. 20.—Bottle, Korea(?), Yi dynasty (1392–1910), Freer Gallery of Art (04.333).

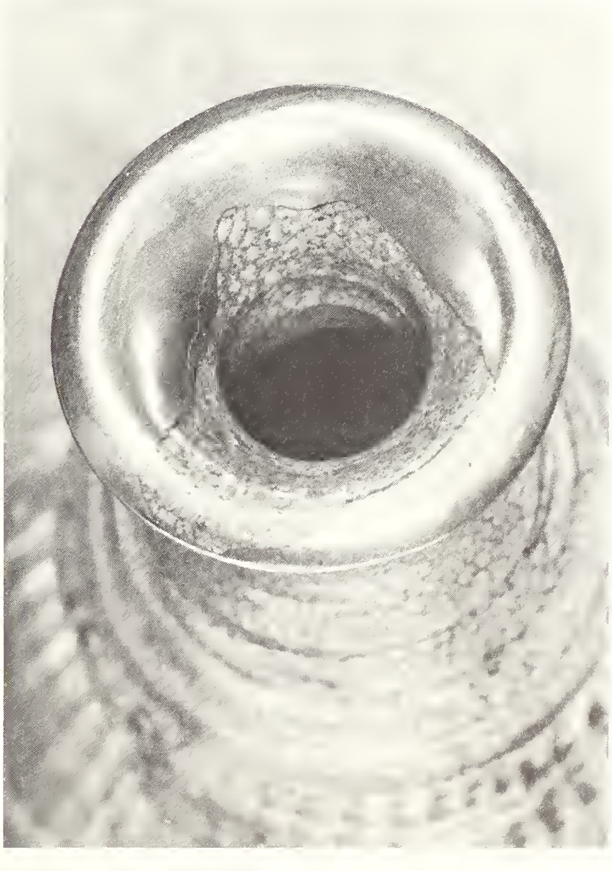


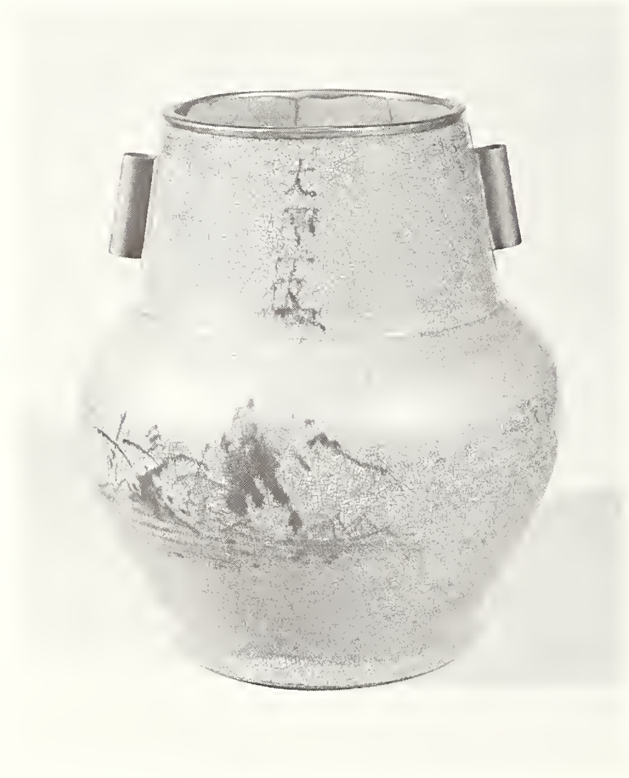
FIG. 21.—Detail, repaired lip of bottle.

urushi and gold. The reconstruction of the foot and lip were done in the *kanshitsu* technique described above. The rich gold surface of the fill was achieved by using several different gold grain sizes. Once the *uwanuri* layer has been completed, large grains of gold are dusted on, then a finer grain is used to help fill voids between larger grains, and finally even smaller grains are used to even off the gold layer. An *urushi* coating called *katame* is applied to the surface as a binder and is finished by polishing (actually burnishing) with charcoal. When this surface is compared with one composed of only one kind of grain or a lesser amount of gold, it becomes evident why this *urushi* artist thought the extra gold was worth the trouble and expense.

A Satsuma ware jar (figs. 22, 23) shows another way in which *urushi* and gold are used in making major structural repairs. Here, the two metal handles are joined to the ceramic using *nakanuri urushi* and metal filings in imitation of the metal fittings. The rim is done with *urushi* and gold in imitation of real metal rims found on some ceramics.

A more unusual type of fill can be done with *urushi* which is finished with a *makie* design. In a Ko Seto jar of the Kamakura period (13th–14th century) (figs. 24, 25), the fine crackle glaze of the piece is beautifully imitated in the repaired lip. The restorer built up his fill in the usual way with *sabi urushi*, *nakanuri* and *uwanuri urushi* and then laid each piece of gold into a black *urushi* layer according to the *hirame* inlay technique; he finished his work by coating the whole piece with black *urushi* and polishing down to reveal the gold as in the *togidashi* technique.

A jar of the Edo period (figs. 26, 27) with



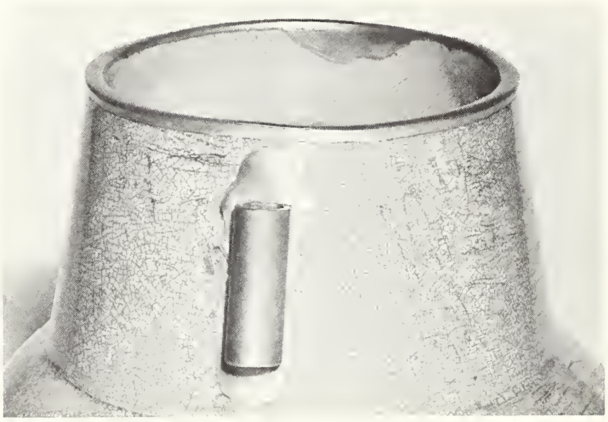
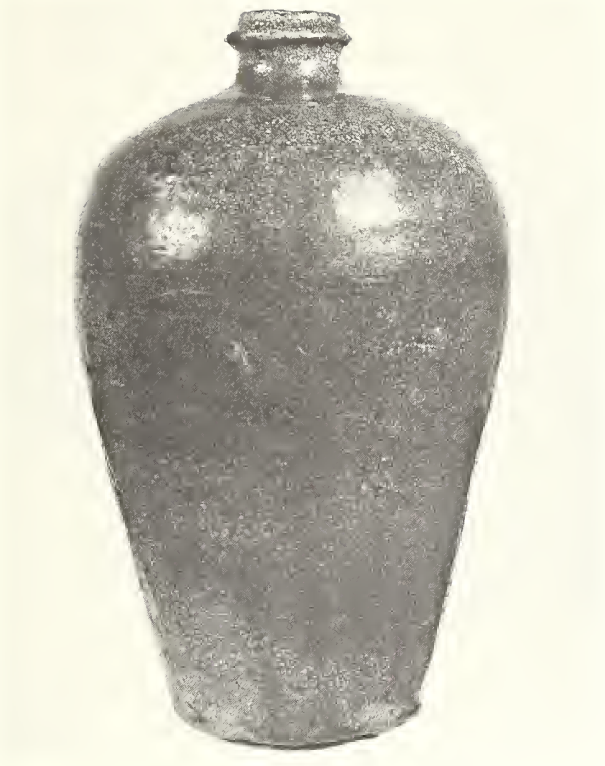


Fig. 23.—Detail, metal fitting and lacquer repaired rim.

Fig. 22.—Jar, Japan, Satsuma ware, Edo period (1615–1868), Freer Gallery of Art (04.148).



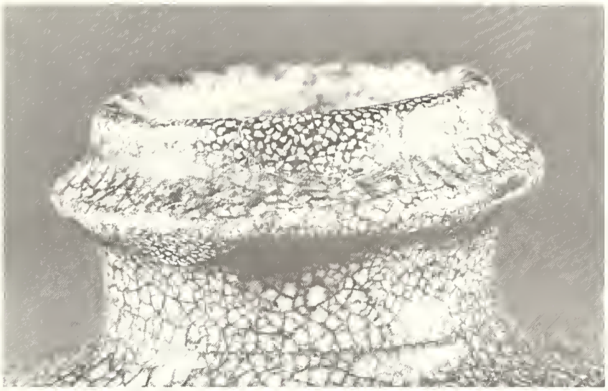
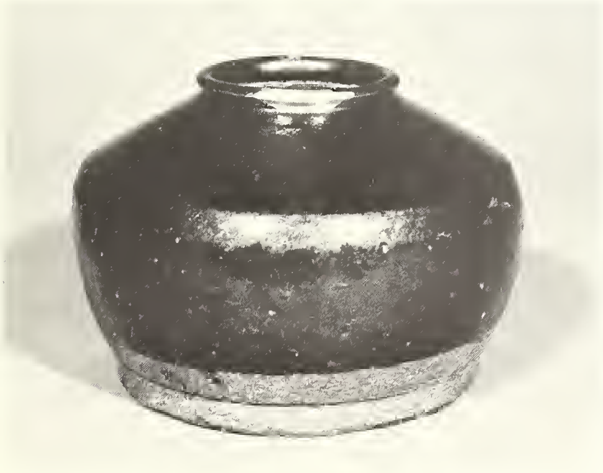


FIG. 25.—Detail, showing repaired lip.

FIG. 24.—Jar, Japan, Ko Seto ware, Kamakura period, 13th–14th century, Freer Gallery of Art (14.14).

an oil spot glaze, also has a fill done in imitation of the glaze. Here the fill is done in exactly the same way as the Ko Seto piece. However, the inlay is done with *kirikane* (each piece of gold is cut out of a sheet of gold leaf into the desired shape) instead of *hirame*. The irregular *hirame* gold is perfectly suited to the irregularity of line and size in the crackle of the Ko Seto ware while the softer, more controlled *kirikane* gold matches



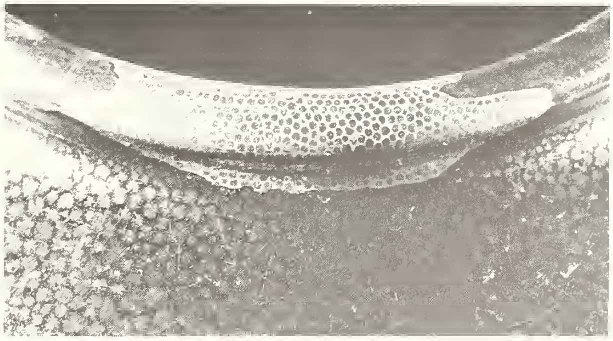
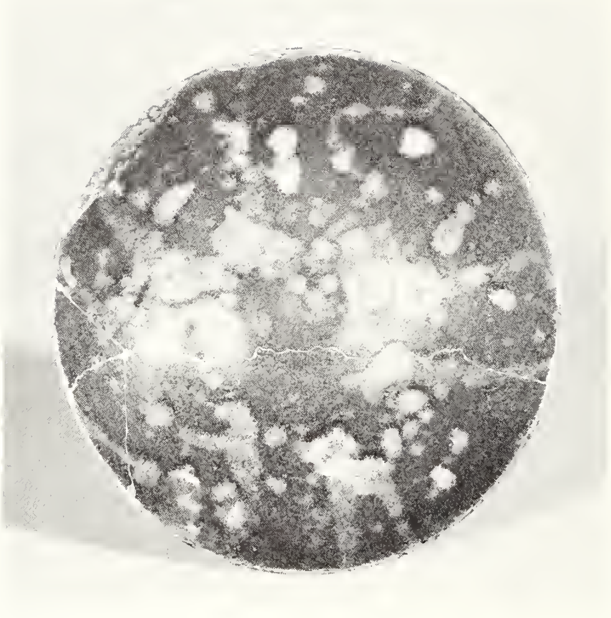


FIG. 27.—Detail, showing repaired lip.

FIG. 26.—Jar, Japan (?) Edo period (1615–1868), Freer Gallery of Art (15.47).



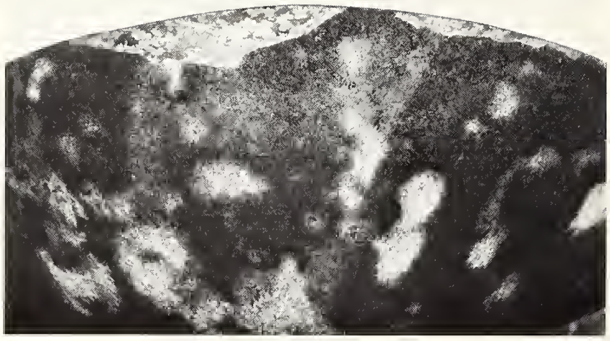


FIG. 29.—Detail, showing repaired lip.

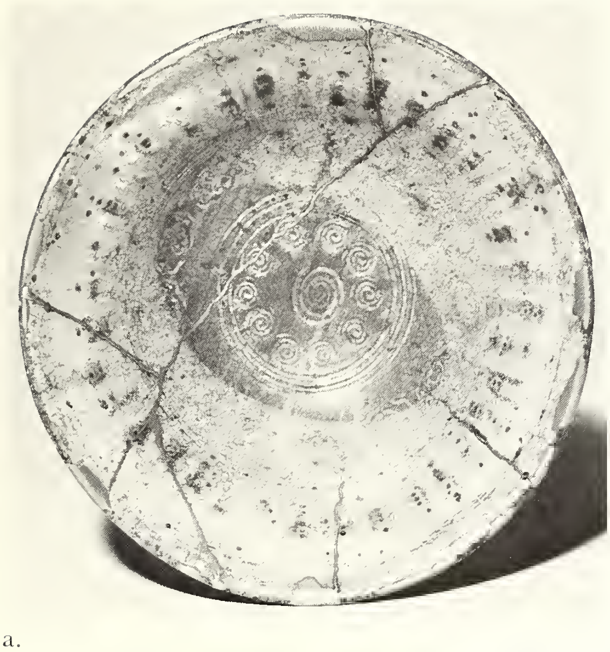
FIG. 28.—Tea bowl, Japan, Seto ware, 16th century, Freer Gallery of Art (00.53).

well with the more muted oil spots of the latter piece. These two fills are perfect aesthetic complements to their pieces.

Not all *makie* finishes on *urushi* fills relate to the glaze as well as the above two examples. A typical repair of this kind is on a 16th century Seto ware tea bowl in the Chinese style (figs. 28, 29). The flowers, applied in *takamakie* on a silver *makie* surface (the silver is now tarnished), have little to do with the glaze except that the delicate gold flowers on silver do not clash with the yellow spots and brown of the glaze. Of special note is the vine of berries that runs along the edge and across the repair. These berry spots have been added subsequent to the original design—they hide an uneven surface which resulted when a section of the repair broke off and was imperfectly rejoined. It is an ingenious solution to a difficult problem, because the uneveness could not be sanded down without damaging the flower design. It is also a nice example of *urushi* used to restore an *urushi* restoration.

An even more unusual example of such an 'out of place' design is on a Japanese Edo tea bowl (fig. 30). The bowl has four losses around the rim, each fill having been finished with a different *makie* design. One section of fill is covered with a flat blue-green gold called *aokin* (fig. 30a). Each of the three other fills (figs. 30b, c, d) have a different relief design. It is hard to ascribe a motive to such a strange combination. One must accept this for what it is—a sampler of what can be done by the *urushi* artist in repairing a ceramic! On this tea bowl we can trace four separate generations of repair. The *urushi* mends were covered with a rough gold such as one gathers from sweepings of leftover gold powders of all sizes and varieties. The smooth yellow gold and *aokin* sections were probably done by two other people, and the three *takamakie* designs were done by yet a fourth hand.

Lacquer restorations on ceramic are not always successful artistically. A Yi dynasty Punch'ŏng ware bowl of the 15th century



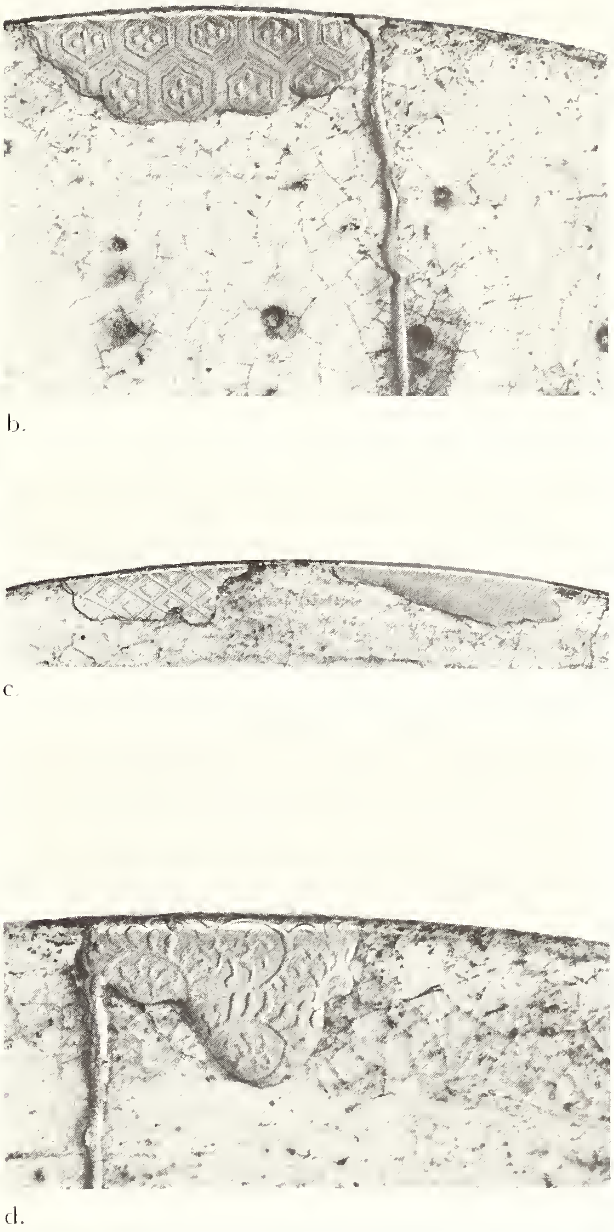


Fig. 30.—Tea bowl, Korea (?), Yi dynasty (1392–1910), Freer Gallery of Art (06.38). a. *aokin*, blue-green gold lacquer repair at the top; b,c,d, *takamakie* repairs

(fig. 31) has a poorly done lacquer repair in questionable taste. The dark line around the fill is *urushi* which was not covered with gold powder. Presumably, the fill was ineptly done from the first, had dropped out, and was re-adhered by a later hand. The bold *takamakie* design has nothing to do with the ceramic glaze and actually tends to overpower the piece. Here, the restoration almost becomes an end in itself.

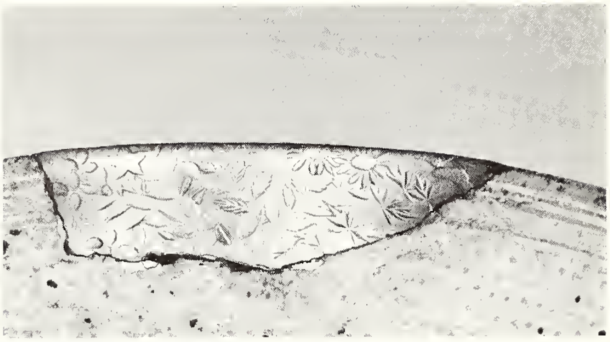


Fig. 31.—Detail, bowl, Punch'ŏng ware, Korea, Yi dynasty, 15th century, Freer Gallery of Art (04.114).

A NOTE ON PROBLEMS IN THE USE OF URUSHI

Among all materials used in conservation, *urushi* is certainly one of the most difficult materials to learn how to use properly. As has already been stated, *urushi* is a highly toxic resin that acts like poison ivy. Most lacquer workers have had to build up an immunity to *urushi* and even then, they must be careful about coming in direct contact with it.

The specific problems of working with lacquer, particularly here in the United States, should be mentioned. *Urushi* needs very special conditions in order to harden, particularly a high level of humidity, around 70–80% R.H. The authors have noticed that *urushi* behaves differently in America than in Japan. Because of the lower humidity, more water must be added to the *urushi* as it is used, the exact amount varying depending on the temperature and humidity in the work area. Also *urushi* ages differently in America, tending to become transparent more quickly than it would in Japan. In order to use *urushi* effectively in a drier climate, artists or conservators must modify their techniques and make allowances for these variations in the behavior of *urushi*.

Urushi, if it is well crosslinked, is insoluble in all standard solvents and is only attacked by such reagents as concentrated nitric acid.[14] In an overview of the kind of damages that are associated with *urushi*, the least likely problem to occur is a chemical breakdown of the *urushi*. This means that *urushi* is irreversible in a chemical sense, and this is a major drawback in terms of an acceptable 'museum quality' restoration. However, it has been the experience of Japanese restorers that *urushi*, if applied judiciously in a repair, can be undone. Time and again, Japanese restorers are able to take apart statues that have been joined with *urushi*, but in this, they have been aided by a thorough knowledge of how the piece was put together originally. It takes a great deal of experience, skill and patience to dismember a statue without damaging the original. Similarly, an old repair on a piece of *makie* can be removed by sanding down to the original surface. This too is a difficult procedure, but these techniques do give a margin of reversibility to what is often thought of as an irreversible process.

URUSHI, TODAY

Today, some lacquer artists still create lacquer wares using the traditional techniques. However, many of the lacquer pieces currently being manufactured in Japan are made with *urushi* substitutes and modified forms of *urushi*, in techniques unknown to *urushi* artists a hundred years ago. While these techniques bring down the cost and time involved in working with *urushi*, they also represent a real loss in quality. It is hard to take shortcuts in the 33 step *roiro* technique without compromising.

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[14] Korschelt and Yoshida, "The Chemistry of Japanese Lacquer," p. 204.

Japanese restorers, too, are beginning to turn away from *urushi* in favor of plastic resins. As these substitutes become pervasive, it must be asked whether there is also a compromise in quality. We do not mean to argue here that *urushi* cannot be successfully replaced in many instances with plastics. *Urushi* is not an inviolable material, without substitutes, but it should be replaced knowingly and with a respect due to a material that has served its function so well for so many centuries. Whatever future *urushi* may have in restoration, it must surely claim a special place in the history of conservation.

ACKNOWLEDGMENT

The authors would like to express their thanks to the entire staff of the Freer Gallery for their encouragement and assistance in every aspect of this report.

GLOSSARY

TYPES OF URUSHI

漆	*Urushi*
固漆	*Katame urushi*–an *urushi* used as a binder for metallic powders
木地呂漆	*Kijiro urushi*–a thin variety of *urushi* that can be used to set down cleavage
木屑漆	*Kokuso urushi*–*urushi* mixed with flour and sawdust
黑漆	*Kuro urushi*–black *urushi*
麥漆	*Mugi urushi*–*urushi* mixed with flour
中塗漆	*Nakanuri urushi*–a grade of *urushi* which has been blackened by iron filings that have been steeped in vinegar
梨地漆	*Nashiji urushi*–a transparent *urushi* used in the *nashiji* technique
糊漆	*Nori urushi*–*urushi* mixed with rice flour
蠟色漆	*Roiro urushi*–a high quality *urushi* used in the *roiro* technique
錆漆	*Sabi urushi*–*urushi* mixed with *tonoko* powder
摺漆	*Suri urushi*–a thin *urushi* used in polishing lacquer

THE STEPS INVOLVED IN MAKING A LACQUER SURFACE

中塗	*Nakanuri*–the intermediate foundation coat
下塗	*Shitanuri*–the basic foundation coat
摺	*Suri*–polishing of the lacquered surface
上塗	*Uwanuri*–the final surface coat

DECORATIVE TECHNIQUES

平蒔絵	*Hiramakie*–'flat sprinkled picture'—the design of metal powders is covered with a thin layer of *urushi*
平目	*Hirame*–an inlay technique using relatively large flat flakes of metal foil
蒔絵	*Makie*–'sprinkled picture'—the general technique in which assorted materials such as precious metal powders are sprinkled on the damp, lacquered surface to create a design.
梨地	*Nashiji*–a technique where a metal powder ground is coated with a transparent *urushi*
蠟色	*Roiro*–the technique employed in producing a highly polished black surface
高蒔絵	*Takamakie*–'raised sprinkled picture'—a *makie* technique producing a design in raised relief
研出	*Togidashi*–'burnished design'—a *makie* technique where the design material is covered with *urushi*, then brought to the surface by polishing through the coating.

DRY LACQUER AND WOOD SCULPTURE TECHNIQUES

一木式寄木造	*Ichiboku shiki yosegi zukuri*–a single block of wood with sections added on
一木造	*Ichiboku zukuri*–single block construction
乾漆	*Kanshitsu*–the technique of dry lacquer
寄木造	*Yosegi zukuri*–multiple section construction

MISCELLANEOUS

青金	*Aokin*–a mixed gold and silver powder which has a blue-green appearance
檜	*Hinoki*–cypress wood
地の粉	*Jinoko*–pulverized powder from unglazed earthen-ware
切金	*Kirikane*–cut gold leaf
膠	*Nikawa*–animal glue
砥の粉	*Tonoko*–powder made from clay (finer than *jinoko*)
角粉	*Tsunoko*–calcined deer's horn ash

NOTES ON THE USE OF COBALT IN LATER CHINESE CERAMICS

By J. C. Y. WATT*

That cobalt was used in earthenware glazes in T'ang times (eighth century) has been known for some time. When R. J. Gettens at the Fogg Museum discovered smalt on a fragment of a mud wall painting from Khara Khoto, judged to date from the eleventh to thirteenth century, he established that cobalt, in the form of smalt, was used as a pigment in Central Asia at least since the thirteenth century.[1] In recent years the problem of the first use of cobalt for underglaze decoration in Chinese ceramics has aroused the increasing attention of students of Chinese ceramic history. The stimulus has come from three separate and related enquiries. First, there is the question of whether porcelain with underglaze blue decoration using cobalt, and underglaze red using copper, was a native Chinese innovation or whether the technique of underglaze blue as well as the cobalt ore itself was an importation from Persia in the first instance—be it in the thirteenth or fourteenth century. Assuming that the blue and white style arose under Persian influence, the second question is the historical one of whether the introduction of a new style of decorating porcelain was a result of the Mongolian rule in China[2] or whether commercial contacts between the Arabs and the Chinese in late Sung times would have been sufficient for the transfer of artistic and technical ideas between the Western Asiatic countries and South China. The third question is an archaeological one of the dating of a class of small blue and white porcelain jars which have been found in considerable quantities in excavations in the Philippines from levels which date from either the late Sung or, at the latest, the early Yüan period.[3] At present, the main obstacle to the attribution of a Sung date to the lowest level of the porcelain site at Pila, Laguna, in southern Luzon, is the occurrence of blue and white jarlets at this level.

These are questions which will take some time to answer. In the end, all theories and speculations must be confirmed by more archaeological data from China, Iran, and South-east Asia. In the meantime, studies and discussions on the cobalt ores used will help to clarify at least one aspect of this intriguing problem.

While significant results have been achieved in recent years in the scientific analysis of the "pigment" on Chinese blue and white porcelain, especially on specimens dating from the early fifteenth century, relatively little progress has been made in relating the results of scientific tests to Chinese records of the use of cobalt in early times, i.e., fifteenth century or earlier. This has been

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[1] Information from Mr. Gettens' manuscript at the Freer Gallery. See also, R. J. Gettens and G. L. Stout, *Painting Materials: A Short Encyclopedia* (New York: Dover Publications Inc., 1966) p. 159.

[2] This theory has been well propounded in Margaret Medley's "Chinese Ceramics and Islamic Design," *The Westward Spread of Chinese Influence*, Percival David Foundation Colloquies on the Art and Archaeology of Asia, No. 3 (London, 1972), pp. 1–10.

[3] The most significant of these excavations so far is the one conducted in 1967/8 in Pila, Laguna, in southern Luzon. See Rosa C. P. Tanazas, *A Report on the Archaeology of the Locsin—University of San Carlos Excavations in Pila, Laguna* (Manila, 1968).

mainly caused by the lack of effort on the part of historians of Chinese ceramics to delve further into Chinese references beyond the well-known passages in the *T'ao-shuo*[a] and *Ching-te-chen T'ao-lu*[b] (hereinafter cited as *T'ao-lu*), both late works (first publication dated 1774 and 1815 respectively), quoting extensively from corrupt late Ming texts, especially in relation to the use of cobalt.

The first part of this paper is an attempt to discuss the scientific results so far attained in a "Chinese context", that is to say, using whatever modern Chinese publication which has a bearing on the subject. The second part is to provide translations of early Chinese texts relevant to the subject with comments and annotation.

Beginning with W. J. Young's experiments in 1949 on Chinese blue glazes and underglaze cobalt,[4] considerable work has been done on the analysis of colouring material as found on Chinese blue and white wares dating from the fourteenth to the present century.[5] All scientific work so far has concentrated on detection and, in some cases, the quantitative measurement of the presence of elements which occur as "impurities" in the cobalt ore(s) used. Discussions of the results of these experiments have so far been based on the assumption that all native Chinese cobalt ores contain manganese as an impurity, and conversely, that the absence of manganese in the cobalt ores used indicates that the ore was imported. Sir Harry Garner goes so far as to state that, "the only form of cobalt ore to be found in China is asbolite. Thus the absence of manganese in cobalt decoration in Chinese ceramics is a certain indication that imported ores were used in manufacture".[6] As this assumption, proposed by Garner, has so far been generally held by all involved in the analytical work, the emphasis of experiments has been to detect presence of manganese and to make measurements of the cobalt/manganese ratio in the compound or mixture of compounds used for blue decoration.[7] This is especially so in the case of experiments performed in Britain. In more recent tests performed at the Conservation Department of the Boston Museum of Fine Arts, detection of the presence of arsenic has been made. Given that arsenic cobalt ores are not supposed to occur in China and that ores such as erythrite ($Co_2(AsO_4)_2 8H_2O$) and cobaltite ($CoAsS$) were known in Persia and recorded by the Persian potter Abū'l-Qāsim in the beginning of the fourteenth century,[8] it would be natural to conclude that the presence of arsenic together with the absence of manganese would confirm the use of an imported ore.

The results of all tests so far, geared as they are to confirm the assumptions set out above, display two salient features. The first is that Chinese blue and white porcelain attributed to the beginning of the fifteenth century and before give no indication of manganese (the low manganese count obtained in some cases can be accounted for by the manganese present in the glaze). Incidentally, tests performed on Persian pieces gave similar readings. In some cases, the presence of arsenic was indicated. The second feature is that all pieces bearing a reign mark of Hsüan-te (1426–35) gave high manganese readings, while those pieces which are attributed by some to the Hsüan-te period and which are unmarked, gave low or nil manganese readings. Assuming the validity of the afore-mentioned assumptions, the results would indicate that imported cobalt was used in all pieces made during the first quarter of the fifteenth century and before. On this point all commentators are agreed.[9] The interpretation of the second feature has given rise to some controversy which is centred around the use of the Hsüan-te mark during the period immediately following that era. The outcome of this controversy affects the relative dating of a certain group fifteenth century blue and white porcelain and need not concern us in the present discussion, unless the authenticity of each and every piece of Hsüan-te marked piece which has been examined is in serious doubt. If one or more of the Hsüan-te marked pieces tested is accepted as of the period, the results of the analytical examination of cobalt would prove that by the Hsüan-te period, a manganese compound occurred in the colouring agent either as a deliberate additive or as an impurity in the cobalt ore used. If the manganese is indeed introduced as part of the Chinese cobalt ore, one must take the Hsüan-te period as the time of the initial use of native Chinese cobalt.

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[4] W. J. Young, "Discussion of Some Analyses of Chinese Underglaze Blue and Underglaze Red," *Far Eastern Ceramic Bulletin*, vol. 2, no. 2, (December, 1949), pp. 19–26.

[5(a)] Stuart Young, "An Analysis of Chinese Blue and White" *Oriental Art*, N.S. vol. 2, no. 2 (1956), pp. 43–47.

[(b)] M. S. Banks and J. M. Merrick, "Further Analysis of Chinese Blue and White," *Archaeometry*, vol. 10 (1967), pp. 101–103.

[6] Sir Harry Garner, *Oriental Blue and White*, (London: Faber and Faber, 1971) Preface to the third edition.

[7] Adrian Joseph, *Ming Porcelains, their Origins and Development* (London: Bibelot Publishers, Ltd., 1971).

[8] J. W. Allan, "Abū'l-Qāsim's Treatise on Ceramics," *Iran*, vol. 11 (1973), pp. 111–120.

However, the assumption that no arsenic cobalt ore exists in China is by no means indisputable. In the first place, the sole occurrence of asbolite to the exclusion of the purer sulphide ores in any region is a highly unlikely event, the latter being often products of transformation or decomposition of more complex cobalt-bearing ores. If one consults the 1956 edition of Chang Shou-fan's[c] *Mineralogy*, the Chinese equivalent of Dana's *Mineralogy*, one finds several arsenic cobalt ores mentioned as occurring in China: erythrite in Chin-hua[d] and Chu-ch'i[e] in Chekiang province; danaite (FeAsS or FeS_2FeAs_2), in which part of the iron has been displaced by cobalt, in Hunan province and Yünnan province; and smaltite or smaltine, $CoAs_2$, which is mentioned as an important cobalt ore and that it occurs in lateritic deposits in many areas in Yünnan.

It should perhaps be pointed out here that further oxidation of smaltite gives rise to erythrite. Now, one of the two chief sites where erythrite occurs in China, Chin-hua in Chekiang, is exactly the source of "best cobalt" according to both the *T'ao-shuo* and the *T'ao-lu*. However, it must be pointed out that previous investigations have identified the cobalt ores occurring in Fukien and Yünnan as asbolite,[10,11] and these are derived from weathering of manganiferous sedimentary rock. This latter type of deposit is closely associated with lateritic deposits.[12]

Before we can obtain more information on the occurrence of cobalt in China and evidence based on the investigation of old mines, it would seem inadvisable to make deductions regarding the importation of cobalt in China solely on the evidence of the presence or absence of arsenic and manganese. From the results so far obtained, a reasonable inference one could make is that manganese was deliberately introduced, probably in the form of asbolite, as a means to control the running of the cobalt in the manufacture of finer pieces in the Hsüan-te period. There are Chinese records dating from at least the sixteenth century describing the mixing of *shih-ch'ing*[h] (probably asbolite) and *Hui-ch'ing*[i] (probably an arsenic cobalt ore) in order to achieve better definition in the painting, and these processes are attributed to even earlier periods. This points to an early sophistication in the use of cobalt ores, but does not necessarily imply that "Chinese" ores (i.e. manganese-cobalt ores) completely replaced "imported" ores (manganese-free ores) by the Hsüan-te period. Indeed, we know from historical records (see below) that cobalt was imported in the Hung-chih (1488–1504) era but no Hung-chih blue and white porcelain has been reported to be free from manganese.

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[9] Sir Harry Garner, "The Use of Imported and Native Cobalt in Chinese Blue and White," *Oriental Art*, N.S. vol. 2, no. 2 (1955), pp. 48–50.

[10] *The Journal of the Geological Society of Tokyo*, vol. 28, no. 337 (1921), pp. 398–400, and vol. 24, no. 350 (1922), p. 483.

[11] Weng Wen-hao[f], *Chung-kuo K'uang-ts'an Chih-lueh*[g] (*Brief Descriptions of Mineral Deposits in China* (Peking: Ti chih chuan pao I Chung, no. 1, 1920).

[12] John S. Vhay, Donald A. Brobst, and Allen V. Heyl, "*Cobalt*." U.S. Geol. Survey Prof. Paper 820 (Washington, D.C., 1973).

Chinese scientists, on the other hand, have pointed out that the "blue" in early Ming blue and white contains a high proportion of iron. In the single published test (wet analysis) on the blue area of a "Hsüan-te" piece, the content of iron in the blue is 2.17% as compared with 0.24% for the cobalt and 0.25% for manganese.[13] This result, according to the authors of the paper, indicates that the cobalt ore was imported because "cobalt ores with such a high iron content and such a low manganese content have so far not been found in our country". The authors further state that: "This fact corroborates historical records that blue material used in Hsüan-te times was imported". The fact is, of course, that if the blue used in the piece tested (which has no mark and is unglazed on the base, indicating perhaps a possible Yung-lo date) was all imported, it could not have contained so much iron either, as erythrite occurs usually with nickel rather than iron and even cobaltite would not contain iron to such a high degree. On the other hand, if danaite (from Hunan and Yünnan) or smaltite (from Yünnan) was used, the high iron content would be expected. It should nevertheless be mentioned in this connection that the *T'ao-shuo*, quoting from late Ming sources, describes a process for removing iron impurities from *Hui-ch'ing* used for underglaze blue (see section IV.ix below). It could be that this process of purifying the cobalt ore was not yet used in Hsüan-te times and therefore early fifteenth century blue and white pieces would exhibit a higher iron content in the blue compared with later pieces.

Nevertheless, even if it cannot be assumed that arsenic cobalt ore must be an imported material or even that imported cobalt must be in the form of arsenic cobalt ores, early records in both Persia and China provide good evidence supporting the theory of the importation of a cobalt ore in China during the early period of manufacture of blue and white porcelain in China. On the Persian side, there is the all important treatise on ceramics by the potter Abū'l-Qāsim, dated 1306, in which he mentions the substance *Sulaimani* being used as a colouring agent which gives the *lājvard* (lapis lazuli) colour. This substance is described as "like white silver shining in a sheath of hard black stone." After taking into account A. H. Schindler's description of the preparation of the cobalt ore from Kamsar, J. W. Allan concludes that "one must therefore assume that Abū'l-Qāsim's 'white silver shining in a sheath of black stone' was asbolane, though such a description fits the sulpharsenide of cobalt, cobaltite, rather better."[14] Abū'l-Qāsim also gives two other ores one of which is identified as erythrite and the other, "an ash-coloured and soft type from Farangistan (roughly Europe)", as again asbolane. On the Chinese side, there is a persistent tradition which records that in the beginning of the fifteenth century (Yung-lo and Hsüan-te) the potters used a cobalt ore called *su-ma-li*[k] blue. There is little doubt that the term *su-ma-li*, which has puzzled commentators for the past fifty years, is one of the various Chinese transliterations of *Sulaimani*. Now, the earliest known written version of this tradition dates from the sixteenth century, a time when the Hsüan-te period had begun to acquire the aura of a golden era of the (albeit not so distant) past. It was possible for late Ming writers, who did not seem to be aware of the exact date of the beginnings of blue and white, to confuse the traditional knowledge regarding the earliest cobalt ore used with that used in the Yung-lo and Hsüan-te periods. As no Ming writer refers to Yüan blue and white, it may be inferred that they regarded blue and white as an innovation of their own dynasty. Thus an imported cobalt, *Sulaimani*, might have been used either in the beginning of the fifteenth century, if we take the records literally, or at an earlier "legendary" period when blue and white was first made. This is an important point to bear in mind in subsequent discussions on the substance *Sulaimani*, especially as its identity is somewhat open to question. If *Sulaimani* is cobaltite, then those in favour of the non-Chinese origin of the earliest cobalt used in Chinese blue and white should argue for the latter interpretation of the sixteenth century texts. On the other hand, if *Sulaimani* is asbolane or wad, then the Chinese tradition regarding the use of imported *su-ma-li* blue in the Hsüan-te period agrees beautifully with the experimental results which show that manganese always occurs in imperial quality pieces with Hsüan-te reign mark. One may indeed go on to reason that the *su-ma-li* blue with its manganese impurity, was introduced for the first time as a refinement to the cobalt mixture to achieve better definition and control in the imperial kilns while the common products, which look early fifteenth century to us and which do not bear the Hsüan-te mark, continued to use some purer (native?) cobalt which was more difficult to control. One could then even provide a plausible explanation as to why so many "provincial" or commercial kilns of the Yüan period could afford to use the purer material for the underglaze blue decoration on cheap mass-produced wares which now are turning up in large quantities from Indonesia and the Philippines. However, such tempting thoughts must remain in the realms of idle speculation before much more detailed knowledge is gained by historical research and more tests on trade wares as well as "imperial" wares.

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[13] Chou Jen[j] et. al, "The purification of cobalt ores and the preparation of pigment for underglaze blue." Chapter 4 in *Ching-te-chen tz'u-ch'i ti yen-chu* (*A Study of the Porcelain of Ching-te-chen*), (Peking: K'o-hsüeh ch'u pan she, 1958).

To return to facts, the earliest unmistakable reference to *Sulaimani* in Chinese records that the present author has come across is to be found in the Wan-li fifteenth year (1587) edition of *Ta Ming Hui-tien*,[1] the General Regulations of the Great Ming. In Chapter 112, it cites regulations decreed in the third year of Hung-chih (1490) concerning the barter value of various "tribute goods" and a certain *su-lai-man*[m] stone is deemed to be worth one roll of fine silk (*chüan*[n]) per two catties (*chin*[o]) of the substance. Another substance, called *Hui-hui shih-ch'ing*[p] was also received as "tribute" during the Hung-chih period and the value, one *kuan*[q] per catty, was considerably lower than that for *su-lai-man*.[15] Assuming that *Hui-hui shih-ch'ing* was a cobalt ore and not azurite (see below), it would appear that cobalts from different sources were known by different names and accorded different values. There is also indication that *Hui-hui ch'ing*[r] also came to China by land through Central Asia. In the thirty-third year of Chia-ching (1554) emissaries from Turfan were recorded to have brought 331 catties and 8 taels (*liang*[s]) of *Hui-hui ch'ing*, and the price was again relatively high, being two taels of silver per catty of the substance.[16] The term *Hui-ch'ing*, or *Hui-hui ch'ing*, occurs in later records of the Ming but there seems to be no more mention of *su-lai-man* after the Hung-chih period. Instead, other transliterations, like *su-ma-li* or *su-ma-ni*[t], were used by sixteenth century writers who referred to such names as those of cobalt blue used in the early fifteenth century. Some sixteenth century writers, like Kao Lien[u] in *Tsun-sheng Pa-chien*[v] and the authors of the *Shui-pu pei-k'ao*[w][17] further identified *su-ma-li* or *su-ma-ni* blue as *Hui-hui ch'ing*, the name by which imported cobalt was known at the time. However, some records can be interpreted as meaning that *Hui-hui ch'ing* was also found *in situ* in Yünnan. Thus the name *Hui-hui ch'ing* must have been associated with certain qualities of the blue in order for the blue from Yünnan to be given the same name as an imported blue.

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[14] Allan, "Abū'l-Qāsim's Treatise."

Even to readers unfamiliar with the subject, it should be clear by now that nothing is clear about the identity or origin of these different cobalt ores so far mentioned. There are two main causes for our non-comprehension of the records from the point of view of the twentieth century scientist. The first is the fact that various cobalt ores were named not according to their properties, but according to their provenance either inside or outside China—except perhaps in the case of *Hui-ch'ing* or *Hui-hui ch'ing*, which increases the confusion as one more variable is introduced. Secondly, confusion is caused by the similarity, or identity, of the trade names for cobalt and those of minerals used for blue pigments in painting. *Shih-ch'ing*, for example, could be a cobalt ore used for underglaze decoration on ceramics or it could be azurite. This lack of discrimination in the use of names was a common foible of people who live in the pre-modern scientific age. The Persians were also guilty of the same imprecision. In Abū'l-Qāsim's treatise, the colouring agent for blue glaze, *Sulaimani*, was also called the *lājvard* stone and was said to produce *lājvard*-colour in glazes. According to J. W. Allan's commentary, *Sang-i lājvard* is the Persian for lapis lazuli.

Yet another source of confusion lies in the very nature of wad, one of the most important cobalt ores used in China, which is a manganese ore with usually a high content of iron which is sometimes substituted by cobalt, in which case it becomes the mineral asbolite or asbolane. Wad, by the name *wu-ming-tzŭ*[x] was confused with another manganese ore *wu-*

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[15] *Ta Ming Hui-tien* (2nd edition, 1587), Chapter 113.

[16] *Ta Ming Hui-tien* (2nd edition, 1587), Chapter 112.

[17] *Shui-pu pei-k'ao* (preface dated 1587). Quoted by Lien-sheng Yang in his review cited in note 18.

ming-i[y], as will be discussed later. This is, however, not a serious problem and neither is the last problem to be mentioned, which is the ease with which Ming and Ch'ing writers of "note-books" (*pi-chi*[z] and *hsiao-shuo*[aa]) freely copied from each other, and the habit of later Ming publishers of freely "editing" the work of well-known authors and market the "edited" version under a different title or with a completely different attribution of authorship.

There is, however, a bonus for the student of ceramic history in the different names used as they will generally indicate the source of the material as well as the period of their use.

In the remainder of this paper, an attempt will be made to review the different names by which cobalt blue was referred to in China and the various texts in which these names occurred. The sources quoted may not be exhaustive, but it is hoped that those sources which are discussed will help to put the various terms for cobalt blue in their historical context.

The following translations, with the exception of II.iii, are all by the author. Square brackets indicate translator's interpolations and explanations, parentheses indicate notes in the original.

I. *Su-lai-man*

In Chapter 112 of the 1587 (fifteenth year of Wan-li) edition of the *Ta Ming Hui-tien*, there is an entry which reads:

> **I.i**—In the third year of Hung-chih, the following regulations regarding [commodity] prices were recommended and approved: for jade-stone, one roll of silk per catty; for stones with jade inclusions, one roll of silk per four catties; for *su-lai-man* stone, one roll of silk per two catties; for *ch'ing-chin*[ab] stone [lapis lazuli], one roll of silk per catty . . .

As discussed above, *su-lai-man* is most likely the Chinese transliteration of the Persian *Sulaimani*. Its value in the year 1490 can be gauged from the values of other stones.

II. *Su-ma-li* and *Su-ma-ni*

The name *su-ma-li* occurs in most records dealing with porcelain manufacture and connoisseurship from about the middle of the sixteenth century onwards. It is most likely that this is a later transliteration for *Sulaimani*. The most well-known of these records is that in the *T'ao-shuo* (preface dated 1774), which is a quote from the *Shih-wu Kan-chu*[ac] (hereinafter cited as SWKC):

> **II.i**—The kiln [products] of the Yung-lo and Hsüan-te periods were made for the Palace. The usual pieces have a skin-pore [surface] and a sweet-white [glaze]. When decorated, *su-ma-li* blue was used. The most treasured [glaze] is the bright-red.

The SWKC was compiled in 1591 by Huang I-cheng[ad] and, like so many similar books of the Ming period, was nothing more than a collection of unrelated facts and here-say mostly culled from earlier books of the same nature, such as the *Ko-ku yao-lun.*[ae] Although none of these books can be regarded as original in any sense of the word, they are useful in transmitting traditional knowledge of connoisseurship and related technical information, especially if the sources are quoted. Huang I-cheng quotes no sources in SWKC, but it is certain that he derived all his entries on porcelain decoration from the *K'uei-t'ien-wai-ch'eng*[af] (hereinafter cited as KTWC) by

Wang Shih-mao[ag] (1536–1588), brother of the more famous Wang Shih-cheng[ah], and himself a scholar of considerable stature. In the KTWC he recounts certain historical events of the Ming period and adds his own comments. The section on porcelain was written when he was a magistrate in Chiu-chiang[ai], near Ching-te-chen, and the part on cobalt blue and glazes served to lead up to his accounts of certain orders for porcelain from the imperial court during the Chia-ching and Lung-ch'ing periods which he thought were unreasonable, excessive, and too great a burden on the country's resources. Nevertheless, this section of the KTWC has provided us with some of the most important records of porcelain manufacture at Ching-te-chen in the sixteenth century. The beginning of this section reads:

> **II.ii**—In the Sung period *Ju*-ware was the foremost [class of] porcelain, and the *Kuan*-ware, which was made in the capital, was second to it. In the present dynasty [a] special [factory is] established at Ching-te-chen of Fou-liang Hsien.[aj] The wares made for the Palace during the Yung-lo and Hsüan-te periods are highly valued nowadays. At that time, the usual [products] have [a] "skin-pore" [surface] and "sweet-white" [glaze]. *Su-ma-li* blue was used for decoration and the most treasured [glaze] was the bright red.

The SWKC shortened the sentence on the value of early pieces made for the Palace and thus somewhat altered its meaning.

A mid-seventeenth century compilation, by a certain Liu Luan[ak], entitled *Wu-shih-ku*[al] (collected in *Chao-tai ts'ung-shu*[am]) contains a nearly identical passage as II.i which must be quoted from SWKC.

Su-ma-li is also known as *su-ma-ni*. Lien-sheng Yang in his review[18] of John Pope's *Chinese Porcelains from the Ardebil Shrine* provides one of the sources of this variant. This is a passage in the *Shui-po pei-k'ao*, "a semi-official publication by Chou Meng Yang[an] and others . . . with a preface dated 1587. It is a kind of handbook prepared by officials of a department in the Ministry of Work [*sic*] for their own reference." Professor Yang's translation of the passage on *Shou-fang Hui-ch'ing*[ao] ("Receipt and distribution of Mohammedan blue") is as follows:

> **II.iii**—The *Hui-hui ch'ing* (Mohammedan blue) is also called *su-ma-ni shih-ch'ing*[ap] (*su-ma-ni* stone blue). It is produced in such places as the Java state and Samarkand. Formerly, it was presented to the court by eunuchs or junior officers (*shê-jen*[aq]) of the [Imperial Bureau] of Investigation *Chin-i wei*[ar] upon their return from a mission to such places as Bengal and the Borneo state in the West Ocean. Recently, it comes entirely from the Turfan barbarians as a tribute. It is stored in the [Imperial Storehouse] *Nei-ch'eng-yün k'u*[as] to be released upon request for use in making porcelains in Kiangsi. If there is a shortage in that province, a memorandum should be sent to the Ministry [of Work] to memorialize a request. The Ministry will dispatch an officer to deliver it [to the province]. It will also send a memorandum to the Ministry of War to obtain tally sheets [*k'an-ho*[at], a kind of pass] for his travel needs on the way. As for the used Mohammedan blue, an ac-

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[18] Lien-sheng Yang, Review of *Chinese Porcelains from the Ardebil Shrine* by John Alexander Pope. *Harvard Journal of Asiatic Studies*, vol. 21 (1958), pp. 214–220.

count book should be kept of it by the office of the Governor and be turned in to the Ministry.

Another reference to *su-ma-ni* occurs in T'u Lung's[au] *K'ao-p'an Yu-shih*[av] (Ch'ien Ta-hsin's[aw] Preface to the 1785 edition says T'u Lung was active in the Lung-ch'ing and Wan-li eras, i.e. from about 1567 to early seventeenth century.)

III. *Su-ni-po*[ax] and *Su-po-ni*[ay]

The *T'ao-lu* (prefaced 1815) was probably the first book to identify (or confuse?) *su-ma-li* blue with *su-ni-po* blue. The *T'ang-shih Ssŭ k'ao*[az] (hereinafter cited as TSSK), the chief source of information on old porcelain for the *T'ao-lu*, contains the following sentence:

> **III.i**—The [imperial] kilns of Hsüan-te used *su-ni-po* blue for the blue decoration, [which] failed by the time of Ch'eng-hua.

In the *T'ao-lu*, this passage becomes:

> **III.ii**—The blue decoration of the Hsüan-te kilns was known as *su-ma-li* blue, [which] became rare in the time of Ch'eng-hua.

In earlier records, *su-ma-li* was never equated with *su-ni-po*. This is not to say that they were necessarily different cobalt ores, but the two names obviously arose out of either different commercial sources and/or different periods. The earliest reference known to the present author to *su-ni-po* blue, from which III.i may be derived, is in *Po-wu yao-lan*[ba] (collected in *Ts'ung-shu Chi-ch'eng*[bb]) by Ku T'ai[bc] in the T'ien-ch'i period (1621–27). It contains the passage:

> **III.iii**—. . . for the blue of the Hsüan-te kilns was *su-ni-po* blue. Later it was used up, and in the Ch'eng-hua period, [it was] all [common blue] *P'ing-teng ch'ing*[bd].

This could, in turn, have been derived, (as pointed out by Nakao Manzō[be] in his important but rather neglected article "Shina tōji no seiryō kō"[bf][19]) from Kao Lien's *Tsun-sheng pa-chien* (published 1591) which says:

> **III.iv**—The blue of the Hsüan-te kilns is *su-po-ni* blue. It was later used up, and by the time of Ch'eng-hua [it was] all *p'ing-teng ch'ing*.

The important difference is that Kao Lien's term is *su-po-ni* rather than *su-ni-po*.

Assuming that *su-ni-po* is not a "corruption" of *su-po-ni*, there is as yet no adequate explanation as to its origin. F. Hirth, one of the earliest scholars to comment on the subject, made the inspired guess that *su-ni-po* is the transliteration of Schneeberg, "under which name the Saxon blue afterwards became famous all over the world"[20]. Some others have tried to explain the term *su-ni-po ch'ing* by separating it nonsensically into *su-ni*, "clay from *su*", and *po-ch'ing*, "blue from *po*".

As to *su-po-ni*, the possible interpretations are equally interesting. Some commentators have again separated a part of the name, in this case, the *po-ni* part, and interpret the terms as "blue from Borneo" (ignoring the *su* part), Borneo being known as *po-ni* in Ming records. Equally fruitlessly, some others have tried desparately to make *su-ma-li* sound like Sumatra. These somewhat far-fetched identifications gained considerable currency in the first half of this century and were persuasive enough to send some geologists and mining engineers searching for cobalt in Sumatra.[21]

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[19] Nakao Manzō, "*Shina tōji no seiryō kō*" in *Tōki Kōza*[bg], 9 (Tokyo: Yuzankaku, 1971).

[20] F. Hirth, "Ancient Chinese Porcelain," *Journal of Royal Asiatic Society*, China Branch, vol. 22 N.S. (1888).

Nakao equated *su-po-ni* with *su-ma-li* and cleverly identified it with the *sa-pu-ni*[bh] stone in T'ao Tsung-i's[bi] *Cho-keng-lu*[bj] and the *sa-po-ni*[bk] stone in the *Ming-shih* "shih-huo chih"[bl]. All these various terms seemed to him to be variants of a transliteration of the word "smalt". He further attributed this theory to a more senior scholar Shioda Rikizo[bm]. He failed to note that F. Hirth in the year 1888 already made the tentative identification of *su-ma-li* (but not *su-po-ni* or *su-ni-po*) with smalt. Incidentally, the smalt theory is currently still held by some writers on porcelain in China today.[22]

E. Bretschneider's note on *sa-pu-ni* in his translation of the relevant passage in *Cho-keng-lu* reads: "*sabuni*, meaning soap-green, is the Persian name of an inferior kind of emerald of a pale colour".[23] If Nakao is right in equating *su-po-ni* with *sa-pu-ni* (*sabuni* in Bretschneider), this opens up yet another possible identification for *su-po-ni*, that it was the name given to a colouring agent in ceramics which produced the same colour as the stone *sabuni*, on the anology that *Sulaimani* was also known in Persia as *lājvard* However, this is unlikely as *sa-pu-ni* is green and *su-po-ni* is supposed to be a blue agent.

In order to complete the record for III.i and III.ii, it ought to be pointed out that the chapter on porcelain in the TSSK, i.e. T'ang Ping-chün's[bp] *Wen-fang ssŭ-k'ao*,[bq] from which the authors of the *T'ao-lu* quoted liberally while feigning to criticise it, is identical word for word with a chapter on the same subject in a small book called *Ku-t'ung-tz'ŭ-ch'i k'ao*[br] ("Studies of Old Bronzes and Porcelain"), published under the authorship of Liang T'ung-shu[bs]. The TSSK, printed in 1778, the forty-third year of Ch'ien-lung, was supposed to be the "original" work of a rich young dilettante from Fukien, while the "Studies of Old Bronzes and Porcelain" was supposed to have been compiled by Liang T'ung-shu, a scholar and senior official, before the year 1778 but published under his own name after this year. Judging from the incongruity of style in the various chapters of the TSSK, it is more than likely that Liang T'ung-shu was the true compiler, although there is also reason to think that copies of a manuscript by a slightly earlier compiler fell into the hands of both parties who then proceeded to print it under their own names.

IV. *Hui-ch'ing*, *Hui-hui ch'ing* and *Hui-hui shih-ch'ing*

Hui-ch'ing has been generally translated as "Mohammedan blue" or sometimes more pedantically as "blue of the Mussulmen". As already hinted at in the introductory section of this article, this term, and its several variants, is fraught with a high degree of ambiguity, which would delight literary pundits but leave those with less imagination a little bewildered. First of all, ambiguity is caused by the fact that *Hui-ch'ing* is also one of the many trade names for azurite in the early seventeenth century. Then, there is the possibility that *Hui-ch'ing* was not only a name given to both imported azurite and cobalt ore (whether erythrite, cobaltite or asbolane) but was later applied to the cobalt ore found in

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[21] However, I am informed by Mr. Dean Frasché that no cobalt has so far been found on this island.

[22] Yeh Chê-min[bn], *Chung-kuo Ku T'ao-tz'ŭ K'o-hsueh Ch'ien-shuo*[bo] (A Simple Account of the Science of Ancient Chinese Pottery Ceramics.) (Peking: Ch'ing-kung-yeh ch'u-pan-she, 1960).

[23] E. Bretschneider, *Mediaeval Researches from Eastern Asiatic Sources* (London, 1937 Edition, reprinted 1967)).

Yünnan which possessed exactly the same, or very similar properties. This is to say, *Hui-ch'ing* was not only a trade name for two different kinds of imports but might have been used in proto-scientific nomenclature.

Hitherto, writers on ceramic history and technology have relied mainly on entries in the *T'ao-shuo* and *T'ao-lu* which are among the passages translated below:

> **IV.i**—During the reign of Cheng-te, the eunuch stationed in Yünnan obtained foreign *Hui-ch'ing* with which fake gems were produced by melting it with [certain] stones. Its price was twice that of gold. When it was learnt that it could be used in the porcelain kilns, it was [so] used and the colour of the products excelled that of older wares.—*T'ao-shuo* quoting from SWKC.

> **IV.ii**—In the [imperial] Chia-ching kilns, *Hui-ch'ing* was much used. When [the] bright red clay [mineral?, colouring agent?] was exhausted, the method [or result] of firing also declined, but *fan-hung*[bt] [overglaze "iron-red"?] could be fired.—*T'ao-shuo* quoting from SWKC.

Both IV.i and IV.ii are ultimately derived from KTWC which contains the following passage:

> **IV.iii**—(continuing from II.ii). By Ch'eng-hua times, the preference was for the bright "five colours" [decoration], but there was as yet no *Hui-ch'ing*. *Hui-ch'ing* is a product of foreign lands. In the Cheng-te period, the eunuch stationed in Yünnan obtained it and used it to produce fake gems by melting it with [certain] stones. Its price was initially twice that of gold. Then it was learnt that it could be used in porcelain kilns, and it proved to be excellent for the purpose. Thus it was that the whole of [Ching-te-] chen used it and the Palace also stocked a certain quantity. As a result [of this new source of blue] the price of blue fell somewhat. In the Chia-ching period, *Hui-ch'ing* was plentiful, but the "bright red clay" [It is not clear whether a pottery clay is meant, or a copper mineral for underglaze red—translator's note.] was exhausted and the method of firing was very different from previous times. Then all of a sudden the Emperor ordered the production of large jars, the largest ones measuring six to seven feet in circumference [Presumably the "Ministry of Works" foot-measure, *Kung-pu ying-tsao ch'ih*[bu], was meant. This measure in Ming times was shorter than the various commercial foot-measures then in use but still somewhat longer than the modern English foot—translator's note] which required large quantities of blue and clay, [There may be a corruption of the original text in the edition used by the translator.] and then hardly two or three pieces out of ten came out complete from the kilns. The expenses for this venture were enormous but no one dared to criticise. When [Emperor] Mu-tsung ascended the throne, he ordered the copying of red-glazed wares of the Hsüan-te period. The Governor-general [of Kiangsi province] pleaded that the [necessary] clay [mineral?] was exhausted but *fan-hung* [overglazed "iron red"?] could be produced. The Emperor reluctantly agreed to this recommendation . . .

Another Ch'ing record derived from IV.iii is the following passage from Liu Luan's *Wu-shih-ku*:

> **IV.iv**—In the time of Cheng-te, a eunuch governor of Yünnan obtained it [*Hui-ch'ing*]. Before this there was none. Although *Hui-ch'ing* was plentiful in Chia-ching times, the "red clay" was exhausted and the method of firing [manufacture] was no longer the same.

Although the author of SWKC, and others quoting from the KTWC, seemed to think that the *Hui-ch'ing* obtained by the eunuch governor (this is a later Ming institution whereby eunuchs were stationed in provinces in addition, or instead of, the governors or inspector-generals) in Yünnan in the Cheng-te period was "foreign" *Hui-ch'ing*, this interpretation could have been caused by their careless reading of two not necessarily related sentences in IV.iii, one saying that *Hui-ch'ing* was (originally imported) from foreign lands, and the other saying that the eunuch obtained it in Yünnan. It could have been that the blue found in Yünnan in Cheng-te time was called *Hui-ch'ing* because of the similarity of its properties to imported *Hui-ch'ing*. This latter interpretation is reinforced by the statement that the price of *Hui-ch'ing* was lowered as a result of the discovery of this new source of supply. If the *Hui-ch'ing* from Yünnan was also imported, there would have been no reason why its price was lower. H. T. Chang in his discussion on *Hui-ch'ing* in his *Shih-ya*[bv] [24] (*Lapidarium Sinicum*) also tended towards this opinion—without mentioning the KTWC.

Incidentally, the record in KTWC is also interesting in relation to the manufacture of "false gems". These must relate to the glass ornaments, especially beads, which were important items of trade in South-east Asia. Archaeological finds of glass ornaments, bangles and beads, from fifteenth century and later sites are known to contain a higher proportion of high-lead glass than finds from earlier sites[25], indicating a greater Chinese participation in glass manufacturing and trade in glass in the later periods, especially in the sixteenth century—assuming that the high-lead glass is of Chinese origin. The record in KTWC on glass production in Yünnan corroborates well with the archaeological evidence.

Nevertheless, *Hui-ch'ing* was certainly (also) imported by both land and sea. Apart from the record in the *Ta Ming Hui-tien*, on the tribute from Turfan, quoted above, an early sixteenth century work recording tributes from the Western Seas (*Hsi-yang*)[bw], Huang Hsing-cheng's[bx] *Hsi-yang Ch'ao-kung Tien-lu*[by] (prefaced 1520), lists both *shih-ch'ing* and *Hui-hui ch'ing* as among the tributes from Sumatra (which does not necessarily mean that it did not have a more westerly origin). As *shih-ch'ing* in this case must be azurite, *Hui-hui ch'ing* has to be cobalt. Both the *Ming-shih* (Chap. 325) and Ku Yen-wu[bz] [26] quote from this entry in Huang Hsing-cheng, and Ku also identified Sumatra with "ancient *Ta-shih*"[cb] or ancient Arabia.

The *Chiang-hsi (Kiang-si) t'ung-chih*[cc] (1732 edition), probably quoting from an earlier edition, states that:

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[24] H. T. Chang (Chang Hung-chao), *Shih-ya* (*Lapidarium Sinicum*). The Geological Society of China, Memoirs, Series B, No. 2 (Peking, 1927).

[25] See, for example, Alastair Lamb, "A Note on Glass Beads from the Malay Peninsula," *Journal of Glass Studies*, vol. 8 (1966), pp. 80–95.

[26] Ku Yen-wu, *T'ien-hsia chün-kuo li-ping shu*[ca], (Lung Wan yü, Ch'eng-tu, 1830).

> **IV.v**—The *Hui-ch'ing* used for pottery was originally a tribute from foreign lands. *Po-t'ang ch'ing*[cd] is produced in Lo-p'ing[ce] district of this prefecture. *Shih-tzŭ ch'ing*[cf] is produced in various areas in Jui-chou[cg]. When *Hui-ch'ing* became popular *Shih-tzŭ* [*ch'ing*] was no longer used.

So much for the origins of *Hui-ch'ing*. We now come to passages describing the properties and use of *Hui-ch'ing*.

The *T'ao-shuo* quotes the following line from *T'ung-ya*[ch] (by Fang I-chih, romantic figure in the Ming-Ch'ing transitional period, scientist, philosopher, man of letters, painter and patriot):

> **IV.vi**—*Hui-ch'ing* is valued because [it produces a] strong colour.
>
> The *T'ao-lu* quoting from TSSK, contains the following passage:
>
> **IV.vii**—(continuing from III.ii) *Hui-ch'ing* was obtained at the time of Cheng-te, and it was used in the imperial kilns of Chia-ching. The variety which when broken with a hammer exhibited cinnabar specks was [regarded as] "best blue", [that which exhibited] silver stars was "medium blue". When pure *Hui-ch'ing* is (was?) used, the colour runs and does not gather. [Therefore] *shih-ch'ing* must be added, either as one-tenth or six quarters [i.e. in proportions of one to ten or four to six]. [The mixture] produces well-defined brush strokes when used for painting and a clear and brilliant colour when used for wash.

This entry in the *T'ao-lu* is a slightly garbled version of the following passage in TSSK:

> **IV.viii**—In the reign of Cheng-te, a eunuch governor of [or eunuch stationed in] Yünnan obtained foreign *Hui-ch'ing*. The [imperial] Chia-ching kilns used *Hui-ch'ing*. The variety which when broken with a hammer exhibited cinnabar specks was [regarded as] "best blue", those with silver stars were "medium blue". When pure *Hui-ch'ing* is [was?] used, the colour runs and does not gather; and when too much *shih-ch'ing* is added, the colour is subdued and not bright. The "best blue" was obtained by adding one *ch'ien* [tenth of a tael or *liang*] to one tael, and when the mixture was in the proportion of four to six it was called "medium blue". When "medium blue" is used for painting, the brush-strokes are well defined; and when the "best blue" is mixed with water [used for wash], the colour is clear and brilliant.

This information in the TSSK is probably derived from local gazetteers (*fang-chih*)[ci] relating to the Fou-liang district in which Ching-te-chen is situated. The following quotations in *T'ao-shuo*, obviously from the same source(s), are more detailed and less confused:

> **IV.ix**—[The kind of] *Hui-ch'ing* [which when] broken up exhibits cinnabar specks was [regarded as] "best blue", those with silver stars were "medium blue". For every catty, three taels of [refined] *ch'ing* was obtained. After the *ch'ing* is broken up, the small pieces were put in water and a magnet was used to attract the impurities; and after sedimentation, five to six *ch'ien* [tenth of a tael] of real [pure] blue was obtain from a catty [of the original mineral].

> **IV.x**—If the *Hui-ch'ing* is pure, the colour runs and does not gather; if too much *shih-ch'ing* is added, the colour is subdued and not bright. "Best blue" is obtained by mixing one *ch'ien* of *shih-ch'ing* to one tael of *Hui-ch'ing*. When mixed in the proportion of four to six, it is "medium blue". When medium blue is used for painting, the brush strokes are well defined. When best blue is mixed with water [used for wash], the colour is clear and brilliant.

Unfortunately, the present author has not been able to consult early gazetteers of the Fou-liang district or of the Kiangsi province to ascertain the earliest occurrence of this description of the two types of *Hui-ch'ing* which bears close similarity to Abū'l-Qāsim's description of the two kinds of *Sulaimani*. As J. W. Allan observes, the description of "white silver shining in a sheath of hard black stone" is most appropriate for cobaltite even if he has concluded that it is more likely to be asbolane.

The record that *shih-ch'ing* was mixed with *Hui-ch'ing* to achieve better definition indicates that the former is likely to be a manganese bearing cobalt ore, or a manganese ore with cobalt content, i.e. wad. At this stage, one is tempted to conclude that the same knowledge and descriptions regarding cobalt ores were known in both Persia and China (perhaps transmitted from Persia to China with the actual substances) and that the variety of *Sulaimani* which is "like white silver in a sheath of hard black stone" is cobaltite after all.

The question of *Hui-ch'ing* or *Hui-hui shih-ch'ing* or just *shih-ch'ing* is complicated by the fact that these terms can also mean azurite. In the *Pên-ts'ao Kang-mu*[cj] (late sixteenth century), Li Shih-chen[ck] identifies *shih-ch'ing* with *pien-ch'ing*[cl] and *ta-ch'ing*[cm]. Under the entry for *pien-ch'ing*, Li Shih-chen explains that:

> **IV.xi**—Su Kung [author of one of the most well known works on materia medica, *pên-ts'ao*, in the T'ang period] says that this is the same [substance] as *lü-ch'ing*[cn], but it is not. Rather, it is what is called *shih-ch'ing* nowadays. It is used by painters. Its colour is blue and does not deteriorate, and is popularly known as *ta-ch'ing*. It is also found in Hupei and Szechuan provinces. The commercial varieties today are *t'ien-ch'ing*[co], *ta-ch'ing*, *Hsi-yi*[cp] [i.e. Western foreigners] *Hui-hui ch'ing* and *fo-t'ou ch'ing*[cq] [i.e. "Buddha-head blue"]; *Hui-ch'ing* is particularly expensive. *Pien-ch'ing*, *ts'eng-ch'ing*[cr], *pi-ch'ing*[cs], *pai-ch'ing*[ct], as mentioned in various *pên-ts'ao* works, all belong to the same family.

The is no doubt that the azurite is meant here. H. T. Chang[27] attributes this same statement to Tu Wan's[cu] *Yün-lin Shih-p'u*[cv] (a twelfth century work) which seems excessively early for this kind of information. In any case, this statement is not found in any of the present-day available editions of the *Yün-lin Shih-p'u*. In H. T. Chang's quotation, the best *shih-ch'ing* is supposed to come from Yünnan. Obviously the author of Chang's source (probably another seventeenth century figure) confused popular information on the two different kinds of *Hui-ch'ing*.

Another late Ming author, Sung Ying-hsing[cw], in his *T'ien-kung k'ai-wu*[cx] (hereinafter cited as TKKW) says:

> **IV.xii**—*Hui-ch'ing* is *ta-ch'ing* from the Western Regions, the better kind is also

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[27] Chang, *Shih-ya*.

> known as *fo-t'ou ch'ing*. Its colour is similar to that produced by the best *wu-ming-i*[cy] after firing.

The two passages IV.xi and IV.xii, coming both from scientific writers of the late Ming, agree well in every detail. Certainly, there was prolific use of a high quality blue pigment, most likely azurite, on religious (both Buddhist and Taoist) images of the late Ming period, not only on the head but on certain parts of the garments.

From the above it can be concluded that both *Hui-ch'ing* and *shih-ch'ing* stood for both cobalt ore and azurite, particularly in the late sixteenth and early seventeenth centuries. However, *Hui-ch'ing* with its foreign connection was always regarded as the superior variety.

The question of *wu-ming-i* will be discussed in the following section.

As a footnote to the above section it may be mentioned that the peculiar hue of violet blue commonly observed on blue and white pieces of the Chia-ching and early Wan-li periods, i.e. the second half of the sixteenth century, which is traditionally described as the colour of "*Hui-ch'ing*", is caused by the relatively high content of manganese in the colouring agent. This point has been made by W. J. Young in the article quoted above.

V. *Wu-ming-i* and *Wu-ming-tzŭ*[cz]

Wu-ming-i is unmistakably mentioned in TKKW as a substance used for underglaze blue decoration. The relevant passage reads:

> **V.i**—The blue material used for painting bowls is always *wu-ming-i* (lacquerers also use this to boil [*tung*][da] oil in order to reduce the water content [of the oil]). This substance does not grow in deep soil but grows on the surface of the earth. The most that one has to dig [to find it] is three feet [rather more than three English feet]. It is found in all provinces and central districts. They are also divided into best, medium and low grades. When it is used, it is first roasted over a charcoal fire, the best grade comes out a kingfisher blue, the medium grade is slightly blue and the low grade an earthy brown. For every catty of the best grade [ore] only seven taels [of blue material] is obtained, the extracts from the medium and low grades are progressively less. For the best fine quality wares, and for painting dragons and phoenixes on imperial wares, the best grade of blue is used, that is why its price is twenty-four taels of silver per *tan*[db] [about 1070 litres if taken as volume measure; or 120 Ming catties, about 72 kilogrammes][28], the price is half for the medium quality and is only three tenths for the low quality kind. In Jao-chou[dc] [Ching-te-chen] the best material used is from the mountains of Ch'ü[-ch'uan][dd] and Hsin[-an][de] districts, and is called Che[-kiang] material; that from places like Shang-kao[df] [in Kiangsi province] is graded medium; and that from places like Fêng-ch'eng[dg] [also in Kiangsi] is graded lowest. To use the material it is roasted and then ground in a mortar (with an unglazed rough inside base), then it is mixed with water for painting. When ground up and mixed [into a paste] its colour is black, [which] changes into blue after firing.

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[28] Calculated according to tables in Wu Ch'êng-lo, *Chung-kuo Tu-liang-heng shih* (History of Measures in China.) (Shanghai: Commercial Press, Shang-wu ying shu-kuan, 1937).

The *Pên-ts'ao Kang-mu*, after the quotes on earlier records of *wu-ming-i*, carries the following explanation by Li Shih-chen:

> **V.ii**—[It is] obtained in the great mountains of Szechuan and Kuang[-si], and is particularly plentiful in Kueilin. There are several hundred of these small black stones in every packet. It looks like *Shê-huang*[dh] [cervantite, antimony ochre?] but is black. It is sometimes also found in the nearby hills. When it is smeared on scissors to cut [the wick of an oil] lamp, the lamp remains burning; when used for boiling crabs, it takes away the fishy smell, and when used in boiling *tung*-oil, it absorbs the moisture.

Analyses of *wu-ming-i*, obtained from apothecaries, since the late nineteenth century have usually revealed that it is either an iron (ferric) oxide with manganese dioxide MnO_2 impurities,[29] or it may be a manganese ore, pyrolusite MnO_2, with iron impurities.[30]

From the description of its properties in the *Pên-ts'ao Kang-mu* and the available analysis data, it would seem that the action of *wu-ming-i* as an oxidising agent and hygroscopic substance depends on the MnO_2 content. The TKKW has perhaps in this case confused *wu-ming-i* with *wu-ming-tzŭ* which has always been one of the names of wad, a manganese ore often with cobalt (and iron and copper) impurities, which becomes *shih-ch'ing* when the cobalt content is high enough, or perhaps even *Hui-ch'ing* when it becomes earthy cobalt or asbolite $CoMn_2O_5 \cdot 4H_2O$.

Wu-ming-tzŭ is mentioned in the 1732 edition of the *Chiang-hsi T'ung-chih*:

> **V.iii**—Both *Shih-chu*[dn] and *wu-ming-tzŭ* are produced in T'ien-tsê Kang[do] and is used in Ching-te-chen for painting porcelain.

Both H. T. Chang and Nakao Manzō quote the seventeenth century lexicon *Cheng-tzŭ T'ung*[dp] as saying:

> **V.iv**—Ching-te-chen takes the blue material from Wu-yüan[dq], one of its names is *hua-shao ch'ing*[dr] [i.e. "Paint-fire blue"] and another name is *wu-ming-tzŭ*.

Previous writers on cobalt, having been slightly misled by the TKKW, often traced the term *wu-ming-i*, assuming that it might have something to do with cobalt, to various sources dating from the Sung period when a *wu-ming-i* was a valued "tribute" from Arabia. Most of these references are to be found in *Shih-ya*.[31] It is now difficult to identify the imported *wu-ming-i* from the Sung descriptions, but H. T. Chang is at least right in saying that *wu-ming-i* is not cobalt and that *wu-ming-tzŭ* is.

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[29] Liu Shou-shan[di], *Chung-yao Yen-chiu Wen-hsien Chê-yao*[dj], (Abstracts of Literature on the Study of Chinese Medicine), (Peking: K'o-hsüeh ch'u pan she, 1963), p. 91 quotes two analyses of *wu-ming-i*; one conducted in 1882 revealed 63.4% Fe_2O_3 and 3.55% MnO_2, and another in 1933 reported that the chief content was iron oxide and did not mention manganese.

The *Chung-kuo Yao-hsüeh ta Tz'ŭ-tien*[dk], (Dictionary of Chinese Medicine), (Peking: K'o-hsüeh ch'u pan she(?) 1956) identifies *wu-ming-i* as the iron ore limonite. Other early twentieth century analyses have also reported iron oxide as the main content.

[30] Chang, in *Shih-ya*, identifies *wu-ming-i* as pyrolusite. Liu Yu-liang[dl] in *K'uang-wu-yao yu Tan-yao*[dm] (Mineral and Elixir Medicines), (Shanghai, K'o-hsüeh chi shu ch'u pan she, 1962), identifies it as a manganese-iron ore which is usually found together with pyrolusite and wad on the surface of manganese mines. He also quotes an opinion that it is an impure pyrolusite. The analysis he quotes shows a 63.3% content of MnO_2.

[31] Chang, *Shih-ya*.

Even if it has no bearing on the present discussion, it may nevertheless be of interest to mention two of the Sung descriptions of *wu-ming-i*. The first is found in one of the *pên-ts'ao* books which records that "it is produced in Arabia. It is found on rocks and looks like lumps of charcoal. The foreigners boil it in oil to produce black lumps and chew them like sweets." The second description is provided by Shen Kua[ds] in his *Meng-ch'i Pi-t'an*[dt] when he records that the real *wu-ming-i* produces a milky streak. (The same property is attributed to another stone called *p'o-so shih*[du] in the *K'ai-pao pên-ts'ao*[dv].) One speculation is that it could be a natural hydrocarbon seep—i.e. a natural tar or "desert varnish".

VI. *Wan-shih*[dw]

One of the more recent names for cobalt ore is *wan-ch'ing*[dx] "bowl blue", as mentioned in the *Shih-ya*. A substance called *wan-shih* is recorded in the *Hsi-yang Ch'ao-kung Tien-lu* as tribute from Java, Ceylon, and Siam. This could be a cobalt ore which had its origin farther afield.

VII. *Chinese cobalt*

It seems that from the seventeenth century onwards only Chinese cobalt ore was used. Both the *T'ao-shuo* and *T'ao-lu* record that cobalt was produced in the provinces of Chekiang, Yünnan, Kwangtung and Kiangsi, and that the ores from Chekiang and Yünnan were of higher quality. The record in *T'ao-shuo* is more detailed:

> **VII.i**—Both for underglaze blue and for blue glaze, blue material is required. [It] comes from the hills in the districts of Shao-hsing[dy] and Chin-hua[dz] in Chekiang province. The gatherers obtain the material in the hills and wash it in the streams to get rid of the attached soil. Large round lumps of a yellowish black colour were the best blue and its name is *ting-yüan-tzŭ*[ea]. After it is brought to Ching-te-chen it is buried in the kiln ground for three days and then taken out and sold after it is washed. The varieties obtained from the hills of Kiangsi and Kwangtung produce a pale colour and do not stand up to firing. They can only be used for coarse ware.

The tradition that the best blue came from Chekiang goes back at least to Ming times. The 1881 edition of the *Chiang-hsi T'ung-chih*, Chapter 49, quotes a memorandum to the Emperor by Hsiao Chin-kao[eb] in the sixteenth century criticising the two eunuchs stationed in Kiangsi province. In it is also mentioned the fact that the best blue, for use on imperial wares, came from Chekiang.

Apart from names for various kinds of Chinese cobalt as mentioned in IV.v, V.iii and VII.i above, others are too many to enumerate here. Often, there are also variants of the same name; *ting-yüan-tzŭ* in VII.i is referred to as *lao-yüan-tzŭ*[ec] in the *T'ao-lu*. Perhaps another detailed study of all the cobalt ores used for ceramic decoration and their provenance in China should be undertaken at a later stage by more able and patient scholars.

For the present purpose, it only remains to record that in the early part of this century, the best blue was considered to be *chu-ming*[ed] or *chu-ming-liao*[ee] from Yünnan province (see VII.ii below) although the Japanese report quoted by H. T. Chang[32] mentions a "very best” grade called *ti-lo*[ef] which was rated even above that of *chu-ming* and two other “best blues”.

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[32] *The Journal of the Geological Society of Tokyo* vol. 28, no. 337 (1921), pp. 398–400, quoted in Chang.

The following extracts from Li Hao-t'ing's[eg] *Ching-te-chen t'ao-t'zŭ kai-k'uang*[eh], “General Description of Pottery and Porcelain of Ching-te-chen” (first published 1937) are offered as a postscript:

> **VII.ii** The best blue material is *chu-ming* from Yünnan, and it is the only usable material for underglaze blue decoration. Formerly, travelling merchants brought this to sell in [Ching-te-]chen. In recent years, because porcelain traders from Yünnan are becoming rare to the point of vanishing, the supply is greatly reduced. What remains is only the old stock of large factories and rich houses, which is only a small quantity. The price rises daily and it is difficult to obtain good quality blue. There is a real danger of the supply running out, and a substitute must be found very soon. The other blue materials are useless for fine painting and can only be used for decorating coarse ware.
>
> It is said that this *chu-ming-liao* is obtained in the hills of Yünnan, and is a natural product. The method of collecting is that the merchant temporarily employs the natives to search the hills after rain. The “raw material” thus gathered consists of stones of a yellowish-black colour, the good ones being round and smooth. The merchant buying this substance should be experienced, otherwise he will not be able to tell. These stones are then packaged and transported to [Ching-te-]chen. Shops dealing in [blue] material must wash it many times after having purchased it and then place it in saggars with paper above and below. After heating in the kilns, it is washed again and crushed, after which it can be sold.—p. 160.
>
> **VII.iii**—For underglaze blue, *chu-ming-liao* is used or *wan-ch'ing* (a cobalt oxide) . . . in recent years . . . *chu-ming-liao* is extremely scarce, the price rising more than ten times, and therefore *chu-ming-liao* is only used for the finest wares. Ordinarily, German and Japanese *wan-ch'ing* is used (the popular name is *yang-liao*[ei] [foreign material]). The colouring effect of *wan-ch'ing* is comparatively strong, that is why it is much used, and the annual import is worth over a hundred thousand *yüan*[ej]. The low grade blue materials are produced in Fu-chou[ek], Kan-chou[el] and nearby areas in this province [Kiangsi]. The colour of *t'u-liao*[em] [earthy material, local material] is not good and is used for low grade porcelain, but some *wan-ch'ing* is mixed with it to improve its colour . . . the prices . . .

Top quality Chinese *chu-ming* blue material	6 *yüan* per catty
Medium quality Chinese *chu-ming* blue material	2 *yüan* per catty
T'u-liao	30 cents per catty
Imported foreign *wan-ch'ing*	50 *yüan* for 60 catties

—p. 102

CONCLUSION

The only conclusion that can be drawn at the moment is that there is no firm conclusion for the time being. The records examined in this paper show that:

(a) Cobalt was imported in the fifteenth century under the name *su-lai-man* and perhaps also *su-po-ni*.

(b) In the sixteenth century *su-lai-man* was referred to as *su-ma-li*.

(c) The earliest record of imported *Hui-ch’ing* was also in the fifteenth century, although this could be azurite.

(d) Cobalt by the name of *Hui-ch’ing* was imported by land and sea in the sixteenth century, although the "foreign *Hui-ch’ing*" from Yünnan in the sixteenth century could have been locally found.

(e) From the description of *Hui-ch’ing* in Ming times, we know that at least some of it was erythrite and some cobaltite. The descriptions also agree well with those for *Sulaimani* in Abū'l-Qāsim, although it can be argued that *Sulaimani* was asbolane (or asbolite).

(f) The knowledge of mixing a manganese bearing ore with purer cobalt ores for better definition of the underglaze painting was known and applied in the Hsüan-te period as shown by recent analysis using x-ray fluorescence spectrometry. This is the period that *su-ma-li* blue was supposed to have been used. This knowledge could have come in with the imported material or arrived at independently by the Chinese potters, and was in any case applied to the production of pieces bearing a Hsüan-te reign mark but not necessarily to unmarked pieces of the same period.

(g) One of the names for a cobalt ore found in Kiangsi province is *wu-ming-tzŭ*, which Sung Ying-hsing, author of the famous *T’ien-kung-k’ai-wu*, might have confused with *wu-ming-i*, which is pyrolusite or a related manganese ore. There is in any case no connection between the *wu-ming-i* of TKKW and that mentioned in various early *pên-ts‘ao* (materia medica) books and in Sung records as having been imported from Arabia or South-east Asia.

(h) From about the end of the sixteenth century and certainly from the seventeenth century onwards there is no more mention of imported cobalt until the beginning of the twentieth century when imported cobalt oxide was used. The halt to the importation of cobalt towards the end of the sixteenth century was obviously caused by the changes in trade patterns and trade partners as a result of the coming of Europeans to Asia.

(i) From about the time of the cessation of the importation of cobalt, the "blue material" produced in Chekiang became increasingly known as the "best blue". This blue could have been erythrite. It is not known when the "Chekiang material" was first discovered and used but it is possible that it could have been among the earliest cobalt ores used. A typical piece of fifteenth century blue and white provincial or "export" ware (fig. 1) in the collection of Mr. Paul Bernat has been shown to contain arsenic in the blue area. It is difficult to believe that imported blue, expensive and hoarded by the official factories, would have been used for this piece in spite of its artistic qualities.

(j) Whether the *Hui-ch’ing* from Yünnan, first found in the early sixteenth century, was a local product or not, the "blue material" from Yünnan became increasingly important from the sixteenth century onwards, and the best was known as *chu-ming* in late Ch‘ing times. Geological and mining surveys so far conducted in Yünnan, have only reported asbolite, although it is not at all unlikely that some purer cobalt ores will be (or were) found.

(k) From the beginning of this century, pure cobalt oxides, as chemical products,

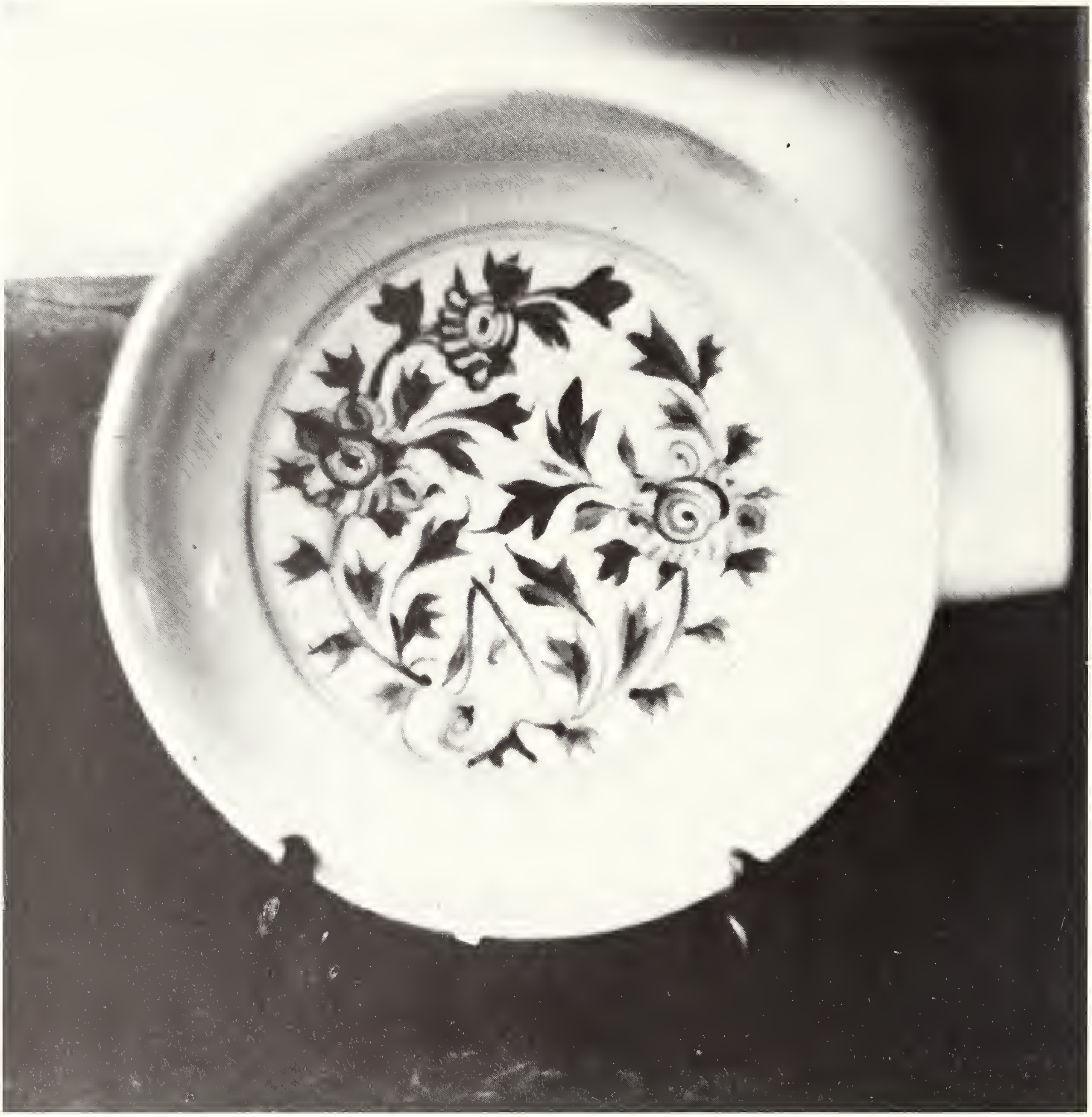

Fig. 1.—Blue and White Dish, Second half fifteenth century. Paul Bernat Collection, Boston. Diameter ~ 14 cm.

are used, sometimes mixed with some local manganese bearing ore.

ACKNOWLEDGMENTS

The material used in this paper was mostly collected in Cambridge, Massachusetts, where the author spent several months in 1974 as a JDR 3rd Fellow. The author wishes to record his gratitude to Mr. Paul Bernat and Miss Elizabeth Jones, who introduced him to the subject of cobalt, to Prof. John Rosenfield and Dr. Eugene Wu who gave him every assistance in using facilities at the Fogg Art Museum and the Harvard-Yenching Library, to Dr. Donald A. Brobst, U.S. Geological Survey, who explained to him the nature and occurrence of different kinds of cobalt ores, to the staff members of the Freer Gallery, especially Dr. Thomas Lawton and Mr. Thomas Chase, who allowed him to consult Mr. John Gettens' notes on the subject when the author arrived in Washington in July, 1974, to learn that Mr. Gettens had passed away.

CHINESE NAMES AND TERMS

a	*T’ao-shuo*	陶說
b	*Ching-te-chen T’ao-lu*	景德鎮陶錄
c	Chang Shou-fan	張守範
d	Chin-hua	金華
e	Chu-ch’i	諸暨
f	Weng Wen-hao	翁文灝
g	*Chung-kuo K’uang-ts’an Chih-lueh*	中國礦產誌略
h	*shih-ch’ing*	石青
i	*Hui-ch’ing*	回青
j	Chou Jen	周仁
k	*su-ma-li*	蘇麻離
l	*Ta Ming Hui-tien*	大明會典
m	*su-lai-man*	速來蠻
n	*chüan*	絹
o	*chin*	斤
p	*Hui-hui shih-ch’ing*	回回石青
q	*kuan*	貫
r	*Hui-hui ch’ing*	回回青
s	*liang*	兩
t	*su-ma-ni*	蘇嘛呢
u	Kao Lien	高濂
v	*Tsun-sheng Pa-chien*	遵生八牋
w	*Shui-pu pei-k’ao*	水部備考
x	*wu-ming-tzŭ*	無名子
y	*wu-ming-i*	無名異
z	*pi-chi*	筆記
aa	*hsiao-shuo*	小說
ab	*ch’ing-chin*	青金
ac	*Shih-wu Kan-chu*	事物紺珠
ad	Huang I-cheng	黃一正
ae	*Ko-ku yao-lun*	格古要論
af	*K’uei-t’ien-wai-ch’eng*	窺天外乘
ag	Wang Shih-mao	王世懋
ah	Wang Shih-cheng	王世貞
ai	Chiu-chiang	九江
aj	Fou-liang Hsien	浮梁縣
ak	Liu Luan	劉鑾
al	*Wu-shih-ku*	五石瓠
am	*Chao-tai ts’ung-shu*	昭代叢書
an	Chou Meng Yang	周夢暘
ao	*Shou-fang Hui-ch’ing*	收放回青
ap	*su-ma-ni shih-ch’ing*	蘇嘛呢石青
aq	*shê-jen*	舍人
ar	*Chin-i wei*	錦衣衛
as	*Nei-ch’eng-yün k’u*	內承運庫
at	*k’an-ho*	勘合
au	T’u Lung	屠隆
av	*K’ao-p’an Yu-shih*	考槃餘事
aw	Ch’ien Ta-hsin	錢大昕
ax	*su-ni-po*	蘇泥勃
ay	*su-po-ni*	蘇勃泥
az	*T’ang-shih Ssŭ-k’ao*	唐氏肆考
ba	*Po-wu yao-lan*	博物要覽
bb	*Ts’ung-shu Chi-ch’eng*	叢書集成
bc	Ku T’ai	谷泰
bd	*p’ing-teng ch’ing*	平等青
be	Nakao Manzō	中尾萬三
bf	Shina tōji no seiryō kō	支那陶磁の青料考
bg	*Tōki Kōza*	陶器講座
bh	*sa-pu-ni*	撒卜泥
bi	T’ao Tsung-i	陶宗儀
bj	*Cho-keng-lu*	輟耕錄
bk	*sa-po-ni*	撒孛尼
bl	shih-huo chih	食貨志
bm	Shioda Rikizo	鹽田力藏
bn	Yeh Chê-min	葉喆民
bo	*Chung-kuo ku T’ao-tz’ŭ K’o-hsüeh Ch’ien-shuo*	中國古陶瓷科學淺說
bp	T’ang Ping-chün	唐秉鈞
bq	*Wen-fang ssŭ-k’ao*	文房肆考
br	*Ku-t’ung-tz’ŭ-ch’i k’ao*	古銅瓷器考
bs	Liang T’ung-shu	梁同書
bt	*fan-hung*	礬紅
bu	*Kung-pu ying-tsao ch’ih*	工部營造尺
bv	*Shih-ya*	石雅
bw	*Hsi-yang*	西洋
bx	Huang Hsing-cheng	黃省曾
by	*Hsi-yang Ch’ao-kung Tien-lu*	西洋朝貢典錄
bz	Ku Yen-wu	顧炎武
ca	*T’ien-hsia chün-kuo li-ping shu*	天下郡國利病書
cb	*Ta-shih*	大食
cc	*Chiang-hsi (Kiang-si) t’ung-chih*	江西通志
cd	*Po-t’ang ch’ing*	陂塘青
ce	Lo-p’ing	樂平
cf	*Shih-tzŭ ch’ing*	石子青
cg	Jui-chou	瑞州
ch	*T’ung-ya*	通雅
ci	*fang-chih*	方志

cj	*Pên-ts’ao Kang-mu*	本草綱目
ck	Li Shih-chen	李時珍
cl	*pien-ch’ing*	扁青
cm	*ta-ch’ing*	大青
cn	*lü-ch’ing*	綠青
co	*t’ien-ch’ing*	天青
cp	*Hsi-yi*	西夷
cq	*fo-t’ou ch’ing*	佛頭青
cr	*ts’eng-ch’ing*	層青
cs	*pi-ch’ing*	碧青
ct	*pai-ch’ing*	白青
cu	Tu Wan	杜綰
cv	*Yün-lin Shih-p’u*	雲林石譜
cw	Sung Ying-hsing	宋應星
cx	*T’ien-kung k’ai-wu*	天工開物
cy	*wu-ming-i*	無名異
cz	*wu-ming-tzŭ*	無名子
da	*tung*	桐
db	*tan*	石
dc	Jao-chou	饒州
dd	Ch’ü-ch’uan	衢川
de	Hsin-an	信安
df	Shang-kao	上高
dg	Fêng-ch’êng	豐城
dh	*Shê-huang*	蛇黃
di	Liu Shou-shan	劉壽山
dj	*Chung-yao Yen-chiu Wên-hsien Chê-yao*	中藥研究文獻摘要
dk	*Chung-kuo Yao-hsüeh ta Tz’*ŭ*-tien*	中國藥學大辭典
dl	Liu Yu-liang	劉友樑
dm	*K’uang-wu-yao yü Tan-yao*	礦物藥與丹藥
dn	*Shih-chu*	石珠
do	T’ien-tsê Kang	天則崗
dp	*Cheng-tzŭ T’ung*	正字通
dq	Wu-yüan	婺源
dr	*hua-shao ch’ing*	畫燒青
ds	Shen Kua	沈括
dt	*Meng-ch’i Pi-t’an*	夢溪筆談
du	*p’o-so shih*	婆娑石
dv	*K’ai-pao pên-ts’ao*	開寶本草
dw	*wan-shih*	碗石
dx	*wan-ch’ing*	碗青
dy	Shao-hsing	紹興
dz	Chin-hua	金華
ea	*ting-yüan-tzŭ*	頂圓子
eb	Hsiao Chin-kao	蕭近高
ec	*lao-yuan-tzŭ*	老圓子
ed	*chu-ming*	珠明
ee	*chu-ming-liao*	珠明料
ef	*ti-lo*	滴落
eg	Li Hao-t’ing	黎浩亭
eh	*Ching-te-chen t’ao-tz’ŭ kai-k’uang*	景德鎮陶瓷概況
ei	*yang-liao*	洋料
ej	*yüan*	元
ek	Fu-chou	撫州
el	Kan-chou	贛州
em	*t’u-liao*	土料

LEAD ISOTOPES IN SOME JAPANESE AND CHINESE GLASSES

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AND MIGDALIA DIAZ[†]

INTRODUCTION

The use of lead isotope ratio determinations for studying ancient objects has become a familiar archaeometric technique.[1] By comparing ratios of lead extracted from objects with ratios of galena ores, it is often possible to identify probable geographical origins of the ores from which the leads were smelted. This, in turn, is useful for deciding where the objects themselves might have been made. Like all archaeometric methods, this one has both its advantages and limitations. The main limitations are, first, that ores from different mining regions occasionally overlap, in the sense that they have similar isotope ratios, and second, that the salvage and reuse of lead sometimes led to mixing of leads from different sources. Important advantages are that only very small samples are consumed in these determinations, the method is insensitive to the chemical history of the objects studied, and it can be applied to a wide assortment of ancient materials which contain lead. Among the materials which have already been analyzed and published are metallic leads, corrosion products, bronzes, silvers, glasses, glazes, and pigments.

Until now, lead isotope data have been published for only a few objects from East Asia. However, an extensive study of lead in ancient Chinese bronzes is now underway at the National Bureau of Standards, and a separate study is underway by a team in

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[1] R. H. Brill and J. M. Wampler, "Isotope Studies in Ancient Lead," *American Journal of Archaeology*, vol. 71 (Jan. 1967), pp. 63–77; R. H. Brill, W. R. Shields, and J. M. Wampler, "New Directions in Lead Isotope Research," *Application of Science in Examination of Works of Art* (Boston: Museum of Fine Arts, 1970), pp. 73–83; R. H. Brill, "Lead and Oxygen Isotopes in Ancient Objects," *The Impact of the Natural Sciences on Archaeology* (London: The British Academy, 1970), pp. 143–164; R. H. Brill and W. R. Shields, "Lead Isotopes in Ancient Coins," *Methods of Chemical and Metallurgical Investigation of Ancient Coinage*, Special Publication No. 8, Royal Numismatic Society (1972), pp. 279–303; R. H. Brill, I. L. Barnes, and B. Adams, "Lead Isotopes in Some Ancient Egyptian Objects," *Recent Advances in Science and Technology of Materials*, vol. 3 (1974), pp. 9–27; R. H. Brill, I. L. Barnes, W. R. Shields, and T. J. Murphy, "Isotopic Analysis of Laurion Lead Ores," *Archaeological Chemistry* (Washington, D.C.: American Chemical Society, 1974), pp. 1–10; B. Keisch and R. C. Callahan, "Lead Isotope Ratios in Artists' Lead White: A Progress Report," *Archaeometry*, vol. 18, part 2 (July 1976), pp. 181–193; C. L. Goucher, J. H. Teilhet, K. R. Wilson, and T. J. Chow, "Lead Isotope Studies of Metal Sources for Ancient Nigerian 'Bronzes'," *Nature*, vol. 262, no. 5564 (July 8, 1976), pp. 130–131.

Japan.[2] In this publication results are reported for a group of very important glass samples from Japan and China.

Readers of this special issue of *Ars Orientalis* will be interested to know that the very first lead isotope determination carried out on a Far Eastern object was accomplished with the help of R. J. Gettens. In 1964 he supplied lead chloride precipitates left over from gravimetric analyses of some Chinese bronzes. Only one of these samples, no. 188, was published,[3] but it served through the years as an anchor point on one end of all our isotope plots and was a constant reminder that another whole part of the world remained to be studied.

In the 1930's, chemical studies by Seligman and Beck and by Seligman, Beck, and Ritchie[4] revealed that early Chinese glasses usually contain very high proportions of lead, and that some of the earliest Chinese glasses, those of the Pre-Han and Han Periods, before 220 A.D., also often contain unusually high contents of barium oxide (BaO). Since then, no report has been published on Chinese glasses with high BaO, but unpublished analyses verifying these findings have been made at The Corning Museum of Glass.

In recent years, one of the authors (KY) carried out extensive examinations and analyses of Japanese glasses and other materials, including objects from the Shōsōin repository in Nara. Several important and greatly revered glasses were among the objects analyzed. The results were the basis of publications dealing with the chemical compositions of Japanese and Chinese glasses.[5] (See discussion below.) Several examples of lead-rich glasses were found, and in fact, high lead-barium contents clearly appear to be characteristic of early glasses from Japan as well as those from China. It was remarked that:

> The geographic distribution of the glasses with the high lead-barium contents is an important problem to be observed in the future, and it may give a clue to the elucidation of trade between Japan and China in the protohistoric period.

It is with this observation in mind that lead isotope determinations were undertaken on a series of 21 of the glasses analyzed, augmented by a few glass samples from the collection of The Corning Museum of Glass and some assorted samples of materials other than glass. The samples were, in most cases, extremely small, the determinations being carried out on powdered residues not consumed in the chemical analyses.[6]

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[2] The first project is being conducted in cooperation with Mr. W. T. Chase of the Freer Gallery of Art. Results by the Japanese team appear in: K. Yamasaki and M. Murozumi, "Lead Isotope Ratios in Ancient Bronze Mirrors and Coins Excavated in Japan (Preliminary Note)," *Kokogaku to Shizenkagaku* (Archaeology and Natural Science), no. 9 (1976), pp. 53–58.

[3] Brill and Wampler, "Isotope Studies . . ."

[4] C. G. Seligman and H. C. Beck, "Barium in Ancient Glass," *Nature*, vol. 133 (June 30, 1934), p. 982; C. G. Seligman, P. D. Ritchie, and H. C. Beck, "Early Chinese Glass from Pre-Han to T'ang Times," *Nature*, vol. 138 (Oct. 24, 1936), p. 721; and C. G. Seligman and H. C. Beck, "Far Eastern Glass: Some Western Origins". *Bulletin of the Museum of Far Eastern Antiquities* (Stockholm), no. 10 (1938) pp. 1–64.

[5] K. Yamasaki, "Chemical Compositions of Ancient Glasses Found in Japan," *Proceedings of the Tenth International Congress on Glass* (Kyoto: The Ceramic Society of Japan, 1974), no. 9, pp. 15–20; and, K. Yamasaki, "Recent Technical Studies of Works of Art in Japan," *Application of Science in Examination of Works of Art* (Boston: Museum of Fine Arts, 1973), pp. 229–234.

[6] The lead isotope ratios were determined at the National Bureau of Standards by procedures routinely employed for small samples. I. L. Barnes, T. J. Murphy, J. W. Gramlich, and W. R. Shields, "Lead Separation by Anodic Deposition and Isotope Ratios Mass Spectrometry of Microgram and Smaller Samples," *Analytical Chemistry*, vol. 45 (1973), pp. 1881–1884.

THE HISTORY OF GLASS IN JAPAN

The early cultural history of Japan is divided into the Jōmon and Yayoi Periods, both named after the types of pottery excavated.[7] No glass has been found in the Jōmon Period (earlier than ca. third century B.C.), but in several sites of the Yayoi Period (ca. third century B.C. to ca. third century A.D.) glass beads have been found. The Yayoi Period is followed by the Kofun Period (Tumulus Period) which spanned from ca. third century A.D. to the seventh century.

In Fukuoka Prefecture, located in the northern part of Kyūshū, there are several important sites of the Yayoi Period. Two are Sugu-Okamoto near Fukuoka city, and Tateiwa, Iizuka city. In these sites with a date of about the first century B.C., large pottery jars were used as coffins. Glass beads, together with other relics such as bronze mirrors, bronze weapons, and shell bracelets were often found inside the coffins.

In the Kofun Period, large mounds were constructed for the burial of the dead, and glass beads have been found in most of these tombs. They are mostly round beads and comma-shaped beads (*magatama*) which seem to have been used as ornaments. According to archaeological findings,[8] the tombs in which bluish green beads made of alkali-lime glass were found are earlier than those which have red, yellow, and dark violet-blue beads as relics; and the beads made of lead glass seem to be found in the tombs of the later age. These glass beads appear to have been imported, as no glassmaking remains have been found.

With the coming of Buddhism to Japan in the sixth century and during the Asuka-Nara Periods (552–793 A.D.), glass vessels were highly esteemed. Small glass bottles were used as receptacles for the most sacred Buddhist relics, each encased in several outer metal receptacles and the whole placed underground on the site where a pagoda was constructed. Examples of these glass receptacles were actually found in the pagodas of Hōryūji, Nara, Sūfukuji, Otsu, and other temples. As far as is known, these bottles are of heavy green glass and are supposed to have been made of lead glass, but no chemical analyses have been made yet because of the religious sanctity attached to them.

By the time of the Nara Period, Japanese glassmaking reached a high level, and thanks to some of the temple and shrine treasuries, in particular the Shōsōin repository, we can today study many glass specimens of the eighth century. In the Shōsōin repository there are beads in quantity: light and dark green, yellow, brown, opaque white, etc.[9] These glass beads are thought to have been made in Japan. This view is supported by a document with the date of 734 A.D. kept in the Shōsōin. This document gives a recipe for making glass beads. According to the document, 386 *Kins* of red lead is melted with 230 *Kins* of "white stone" to make glass beads. At that time, one *Kin* corresponded to about 450 grams. Provided that "white stone" was pure quartz, the chemical

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[7] For a general history of glass in Japan written in English see: D. L. Blair, *A History of Glass in Japan* (Tokyo: Kodansha International and The Corning Museum of Glass, 1973).

[8] Yukio Kobayashi, *Zoku Kodai no Gijutsu* (Ancient Technology, continued volume) (Tokyo: Hanawa Shobō, 1959).

[9] *Shōsōin no Garasu* (Glass Objects in Shōsōin), ed. Shōsōin Office (Tokyo: Nihon Keizai Shinbun, 1965) Report of the special investigation carried out by Yoshito Harada, Kazuo Yamasaki, Jo Okada, and Kozo Kagami.

TABLE 1

Chemical Analyses of Some Japanese and Chinese Glasses
(In weight percent)

	1520	1521	1523	1524	1525	1526	1527	—	1528	1529	1530	1532
	China		Sugu, Fukuoka	Tateiwa, Fukuoka		Uki-Kunden, Saga	Fukuoka	China (Seligman et al.)	Miyajidake shrine, Fukuoka			Takakura Nagoya
	ritual *pi* disk	ritual *pi* disk	tubular bead	rod-like bead	tubular bead	tubular bead	bracelet	cicada	round bead	round bead	flat glass	round bead
	dark green	dark green	dark green	dark green	dark green	dark green	dark green	colorless	dark green	dark green	dark green	dark green
SiO_2	36	36	38	37	68	38.9	25.4	34.42	29.2	21.9	23.1	23.9
Al_2O_3	0.36	0.13	0.35	0.52	2.3	0.56	0.44	0.76	0.08	0.33	0.70	0.05
Fe_2O_3	0.13	0.07	0.29	0.14	0.90	0.30	0.19	0.16	0.08	0.07	0.07	0.34
CaO	1.6	0.01	1.1	0.50	†	2.83	tr	0.12	tr	0.23	0.05	0.35
BaO	14	13	14	16	†	7.59	nd	12.58	nd	nd	nd	nd
MgO	0.16	0.08	0.15	0.20	0.16	0.95	tr	0.35	0.05	0.18	0.14	0.03
Na_2O	1.65	1.96	3.90	2.65	0.27	4.68	0.42	4.32	0.04	0.26	0.04	0.05
K_2O	0.26	0.17	0.19	0.50	0.12	0.21	0.17	1.02	0.04	0.91	0.05	0.06
PbO	46.1	48.5	38.5	40.8	6.95	43.5	70.8	43.20	71.2	75.6	74.0	73.9
CuO	0.88	0.84	0.78	0.76	0.32	0.42	1.67	—	0.28	0.38	0.42	0.19
Ag_2O	0.05	0.05	0.01	0.05	†	†	0.52	—	†	†	†	†
Method	a	a	a	a	a	w	w	w	w	w	w	w

Table 1 (*continued*)

Chemical Analyses of Some Japanese and Chinese Glasses

	1536	1537	1538	1539	1541	1542	1543	1544	1545	1546		1547
	Shōsōin repository Nara				Yakushiji, Nara		Seiryōji, Kyoto	Tamayu, Shimane	Nagasaki	Shinooka kiln, Aichi		Shōsōin, Nara
	round bead	round bead	round bead	round bead	round bead	round bead	glass bottle	glass lump	glass tube	glazed dish		red lead
	brown	reddish brown	dark green	white opaque	dark green	yellow	bluish violet	bluish green	bluish green	green		yellowish red
SiO_2	23.7	24.8	24.7	32.8	28	28	30.1	50.6	36.9	36.1	H_2O	0.06
Al_2O_3	0.13	0.30	0.31	0.19	0.025	0.061	0.30	7.85	0.03	4.3	Insol.	0.35
Fe_2O_3	0.97	0.69	1.08	tr	0.22	0.19	0.28	0.79	0.26	1.1	Pb	0.82
CaO	0.26	0.26	0.71	tr	0.07	0.32	tr	8.73	0.41	tr	PbO	70.9
BaO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd		
MgO	0.57	0.36	0.06	tr	0.02	0.02	tr	tr	0.03	tr	Pb_3O_4	26.2
Na_2O	0.10	0.11	0.12	0.19	$\dagger$	$\dagger$	0.42	14.7	0.13	0.3	Fe_2O_3	0.01
K_2O	0.18	0.10	0.09	0.19	$\dagger$	$\dagger$	11.2	2.15	8.47	0.5	Al_2O_3	0.23
PbO	72.6	73.6	71.9	66.0	70	66	55.8	13.2	51.0	57.0	CaO	0.18
CuO	0.19	0.55 (Cu_2O)	1.44	0.35	0.54	0.10	1.75	0.66	1.58	1.1	MgO	0.03
Ag_2O	$74^{\dagger\dagger}$	$78^{\dagger\dagger}$	$344^{\dagger\dagger}$	$57^{\dagger\dagger}$	0.14	0.16	0.06	$\dagger$	0.095	$\dagger$	CuO	0.03
Method	w	w	w	w	a	a	w,a	w	w,a	w		w

Most of these analyses were originally reported in: K. Yamasaki, "Chemical Compositions of Ancient Glasses Found in Japan," *Proceedings of the Tenth International Congress on Glass* (Kyōto: The Ceramic Society of Japan, 1974), no. 9, pp. 15–20; and, K. Yamasaki, "Recent Technical Studies of Works of Art in Japan," *Application of Science in Examinations of Works of Art* (Boston: Museum of Fine Arts, 1973), pp. 229–234.

a—Analyses by atomic absorption, flame photometry, and emission spectrography.

w—Analyses by wet chemical methods.

†—Detected spectrographically, but not determined.

††—Activation analyses reported as ppm Ag.

tr—Trace.

nd—Not detected.

composition of the glass beads obtained would have been approximately: PbO, 62 percent and SiO_2, 38 percent. These values are close to the actual compositions of glass beads preserved in the Shōsōin, as found by chemical analyses (Table 1). These glass beads were used mostly in temples.

The use of glass beads as ornaments continued in the later Nara Period (eighth century), but in the following Heian Period (794–1185 A.D.) the production of glass beads decreased considerably. The reason is not clear, but changes in customs and manners may have had an effect. In the 13th century, glass bead making in Japan is supposed to have been almost entirely suspended.

In 1570, after the opening of the port of Nagasaki to Portuguese trade, European glassmaking techniques were adopted, probably by way of China. Some of the glass objects made in Nagasaki, Kagoshima, Osaka, and Edo (Tokyo) in the 18th and 19th centuries still exist.

CHEMICAL COMPOSITIONS OF JAPANESE GLASSES

Most of the glasses included in the present investigation were analyzed chemically by one of the authors (KY). Wet chemical methods, flame photometry, and atomic absorption were used. The results are presented in Table 1, and a few notes on the various types of glass are listed here.

(1) Glasses of the Yayoi Period (ca. third century B.C. to ca. third century A.D.). Glasses excavated at the sites of Sugu-Okamoto and Tateiwa were analyzed (nos. 1523 and 1524) along with a glass bead (no. 1526) of the Yayoi Period excavated at Uki-Kunden, Saga Prefecture. The chemical compositions of these glasses are closely related to those of two Chinese ritual disks of the Warring States Period and also to that of a glass cicada studied by Seligman *et al.* Because such high concentrations of BaO have previously been found only in Pre-Han glasses, it is highly probable that these beads, nos. 1523, 1524, and 1526, were made from imported glass lumps or glass objects made in China in Pre-Han times. A sandstone mold used for casting comma-shaped beads (*magatama*) and a glass *magatama* with a high BaO content, which fits in this mold, were found in another site of the same period in Fukuoka Prefecture.[10] This indicates that trade in glass might have been conducted between Japan and China in the Yayoi Period.

(2) Glasses of the Late Kofun Period (ca. sixth to seventh century A.D.). Three beads found in a tomb near the Miyajidake shrine, nos. 1528, 1529, and 1530, and another bead found in the Takakura tomb in Nagoya (no. 1532) were analyzed. These are all green beads which contain lead but do not contain BaO.

(3) Glasses of the Nara Period. Four glass beads preserved in the Shōsōin, nos. 1536, 1537, 1538, and 1539, were chemically analyzed. Minute quantities remaining after the chemical analyses were used for lead isotope studies. The glass beads found in the interior of the pedestal of the main Buddhist figure of the Yakushiji Temple, Nara, (nos. 1541 and 1542) were also analyzed. The Shōsōin and Nara glasses all contained lead but no BaO.

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[10] Sueji Umehara, *Nihon Jōko no Hari* (Ancient Glasses in Japan), *Shirin*, vol. 43 (1960), p. 1.

(4) Glasses and pottery glazes of later periods. As an example of the Heian Period glass, a fragment of a bottle (no. 1543) found within the image of Sakyamuni of the Seiryōji Temple, Saga, Kyoto, was analyzed. This image was made in China in 985 A.D. and brought to Japan in 987 A.D. Therefore, this glass bottle was made in China at this date or earlier.

INTERPRETATION OF THE RESULTS

For readers who are not specialists in the physical sciences and who may hesitate to become immersed in a subject which appears highly complicated, we can offer a word of encouragement. While the instrumentation of mass spectrometry and its associated computer components are extremely complex, as are the geochemical theories governing the isotopic differences among lead ores, the interpretation of the results of this sort of study can be followed without becoming involved in these complexities. The results of the research come in the form of numbers, which serve as indices characterizing galena ores from different mining regions. Then, while keeping in mind the limitations mentioned at the outset, comparisons are made among the samples. Ideally, one hopes to find matches not only among groups of objects, which might thus imply a common origin, but also among objects and ores, so that specific sources of the leads can be identified for given objects.

Fortunately, isotope data are available on some Japanese ores, but we do not have data on many galena ores from China. Therefore, it was realized that a comprehensive interpretation of these data will not be possible until sometime in the future.

Figures 1 and 2 summarize the results of analyses of some 600 ancient leads and galena ores which have been analyzed over the past 15 years. The ellipses drawn in and labeled L, E, X, and S are included to show certain well-defined types of lead which have been encountered time and again in the study of objects from the West and the Middle East. The letters represent types of lead from the Laurion mines in Greece (L), leads from England (E), leads of overlapping types from Italy and the Levant (X), and overlapping leads from Spain, Wales, and Sardinia (S). These letter determinations should not be taken too literally, because of the overlapping of leads from different regions. They serve only as convenient reference points. The extended ellipse towards the lower left encloses data from ancient Egyptian kohls, faience, and glass, as well as some Egyptian ores.[11]

The few small unlabeled crosses are as yet unpublished results on leads from Chinese bronzes. They span virtually the entire range of leads observed from all other sites studied, with data from the present study ranging outside. In fact, the highest and lowest points on the graph are, respectively, a Chinese glass sword terminal (1009) and a Chinese white lead pigment (501). This variability in isotopic composition reflects the great variability within the geological ages and types of galenas occurring in China. This is not surprising, because, after all, China covers an area as great as that covered

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[11] There are various systems for plotting lead isotope data. We have elected regularly to plot Pb^{208}/Pb^{206} vs. Pb^{207}/Pb^{206}. For most situations this appears to separate leads which differ from one another and group those which are similar. A second plot of Pb^{204}/Pb^{206} vs. Pb^{207}/Pb^{206} is always made, and occasionally this serves to distinguish between leads which appear marginally similar on the first plot. An example is mentioned towards the end of the text.

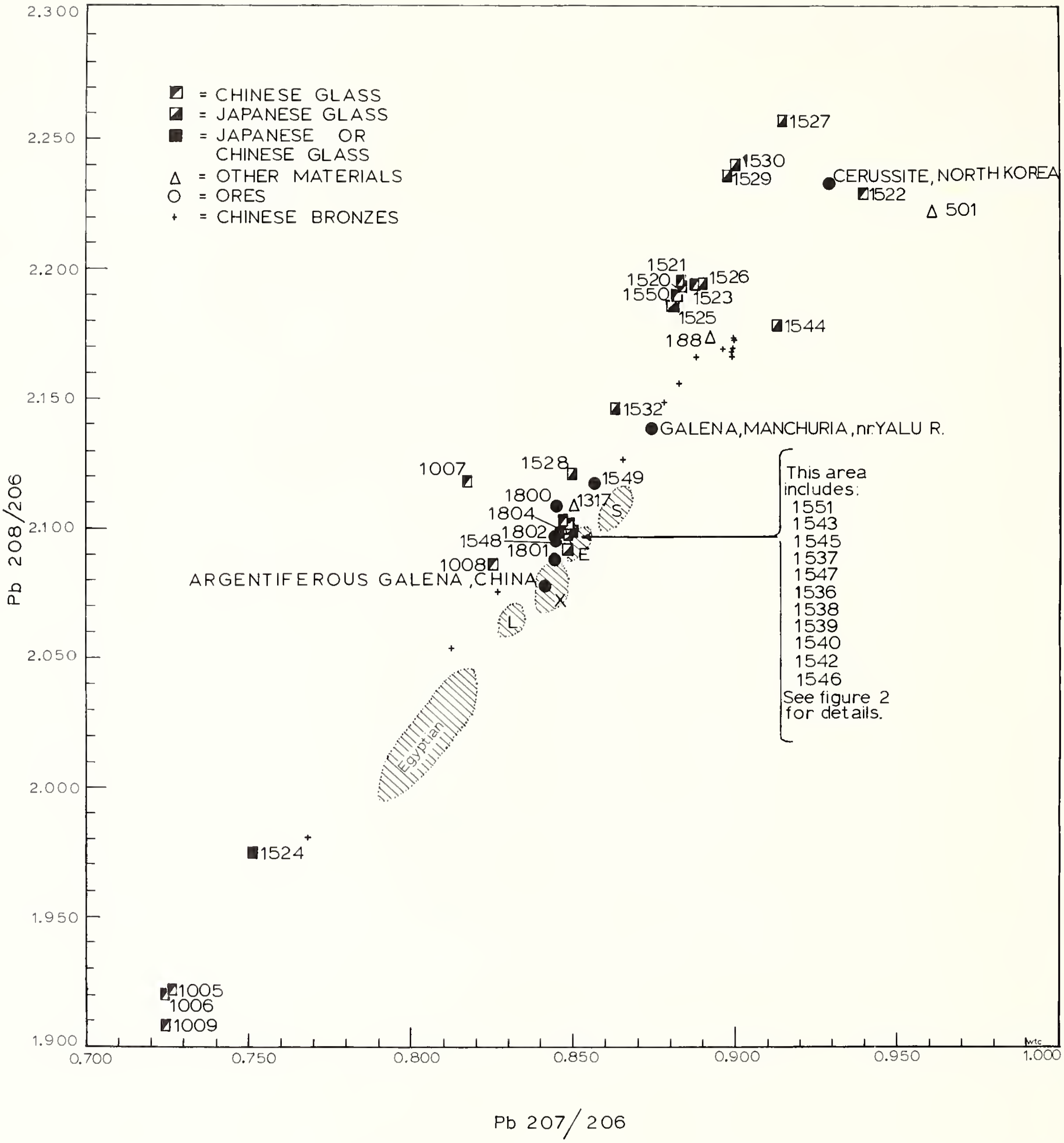

Fig. 1.—Lead isotope data for samples studied in this research, plotted with ellipses summarizing the results of approximately 600 samples from more westerly sources and unlabeled points showing data for Chinese bronzes. The lead isotopic ratios as measured on samples of this type are normally considered to be accurate to ± 0.2 percent. In general, the measurements are probably much better than this. The above limit is considered to take in all possible sources of error including that which might be caused by contamination during chemical processing, variations in the chemical blank, and all of the sources of error in the mass spectrometric measurements.

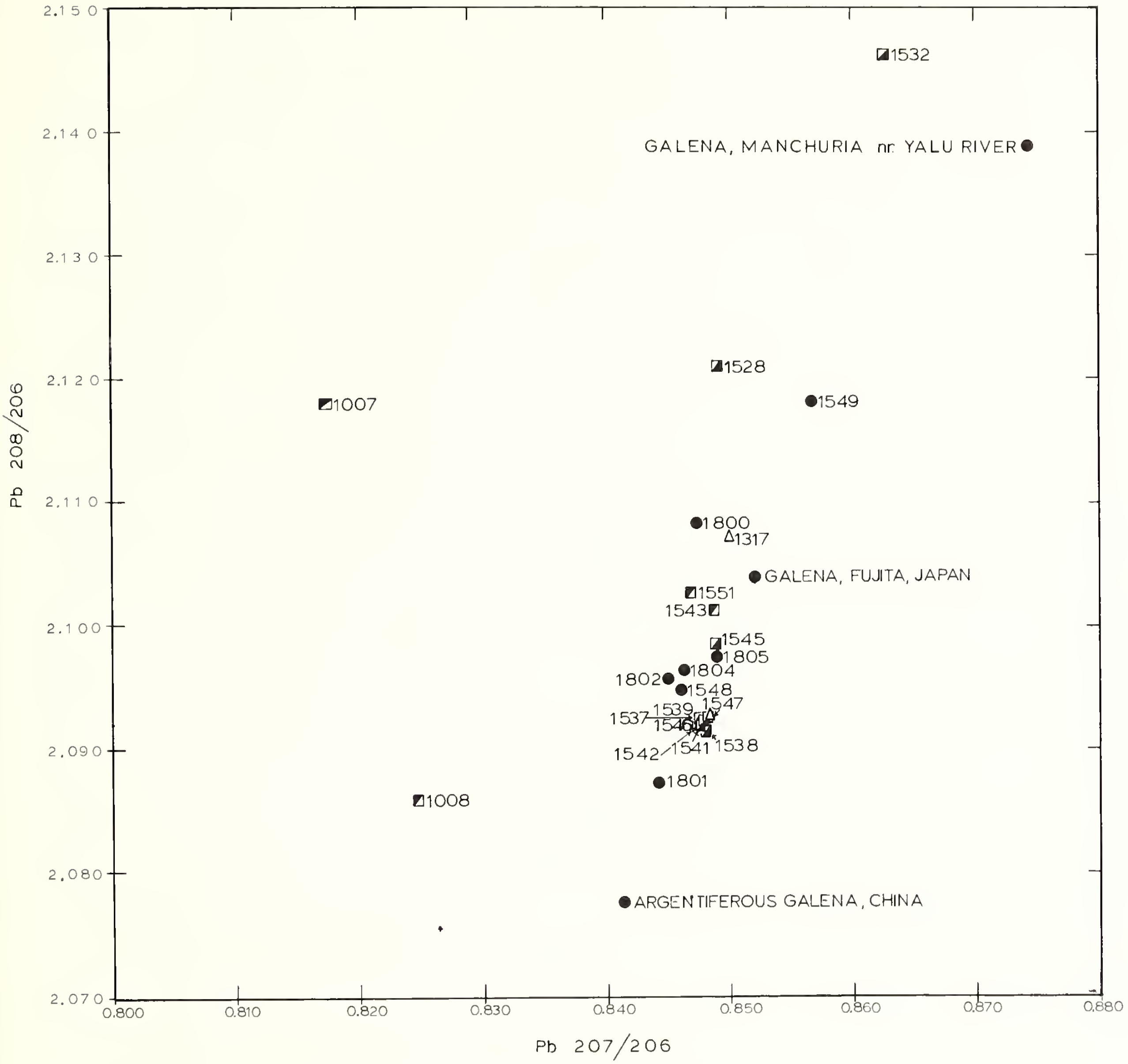

FIG. 2.—A portion of Figure 1 on an expanded scale.

by the sources of all 600 of our other samples put together.

Unfortunately, data on the provenances of most Chinese bronzes are not presently available, and so, it is still too early to sort out the various clusters of points observed according to geographic locations. Eventually, however, we expect this will become possible. It is against this overall background of known isotopic data for leads previously obtained that the results on the Japanese and Chinese glasses must be examined.

In all, 40 samples were analyzed for this study. Detailed descriptions are given in the

Catalogue of Samples, and the data are reported in Table 2. On the basis of the isotopic compositions, they divide themselves into three distinctly different groups. These fall towards the upper right-hand corner of the graph, in the lower left-hand corner, and in the middle. (As usual, a few stray samples fall in between.) Within these three groups some tight clusters of points indicate leads from a single mine, or very closely related deposits. The samples are arranged below in a tabular form indicating these groups and clusters.

In the pages which follow, the results are discussed in terms of the individual samples and groupings. Interpreting data in this fashion can become difficult, but it is a necessary part of the process. The interpretation becomes confusing because one must simultaneously consider the lead isotope data, geographical origins, chronology, and in this instance, chemical compositions of the samples.

GROUPING OF SAMPLES ACCORDING TO ISOTOPE RATIOS

In Table 3 the samples are arranged in approximate order of increasing Pb^{207}/Pb^{206} ratios. The points closest to one another in the list are nearest neighbors on the graph. Where transitions occur within a group, they are separated by an asterisk (*). A double asterisk (**) indicates a more distinct separation. A dagger (†) indicates specimens whose results present some difficulty of interpretation. The samples are glasses unless otherwise noted, and BaO indicates known high-BaO glasses.

The first broad group lies in the upper right-hand section of Figure 1, the part corresponding to geologically older leads. Previously, we had found only a few leads or ores with such high ratios. All came from China or such high ratios. All came from China or India, except for one which is believed to have come from Central Asia. Altogether, this group contains eleven new leads, six of which are clustered, and the other five of which are somewhat scattered. The cluster of six are very likely to have come from the same mining regions, but probably not exactly the same mine unless that mine cut through different contact levels. As closely related as these points are, the difference between the pair of points to the right and the four points to the left is, in fact, greater than the range among a total of 17 ores from galleries and shafts in the Laurion deposits.[12] But nonetheless, the six leads here (nos. 1520, 1521, 1523, 1525, 1526, and 1550) almost certainly came from the same mining region. On the basis of strictly *a priori* reasoning, all six of the glasses have Chinese attributions even though three were excavated in Japan. The assigned dates are the Warring States Period for glasses (in Chinese chronology) and the early Yayoi Period for the tombs excavated (in Japanese chronology). In all, this spans about four centuries (ca. fourth century B.C. to the first century B.C.). These results are especially interesting in that all the glasses have the high PbO-high BaO composition characterizing the earliest glasses of the Chinese manufacture. This means that glasses made in China during the Warring States Period were brought to Japan and remelted for making beads. These beads were used as ornaments and ultimately were buried in Japanese tombs of the Yayoi Period. One of the samples, no. 1550, is an eye-bead of the general type

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[12] Brill, Barnes, Shields, and Murphy, "Isotopic Analysis . . ."

TABLE 2

Lead Isotope Data for Samples Included in Study

Sample No.	Pb^{208}/Pb^{206}	Pb^{207}/Pb^{206}	Pb^{204}/Pb^{206}
Japanese and Chinese Glasses			
1005	1.9211	0.7257	0.04516
1006	1.9203	0.7253	0.04509
1007	2.1178	0.8168	0.05167
1008	2.0859	0.8245	0.05239
1009	1.9081	0.7247	0.04511
1520	2.1930	0.8846	0.05697
1521	2.1939	0.8840	0.05691
1522	2.2295	0.9389	0.06172
1523	2.1933	0.8881	0.05730
1524	1.9748	0.7507	0.04689
1525	2.1880	0.8819	0.05667
1526	2.1939	0.8898	0.05742
1527	2.2570	0.9145	0.05854
1528	2.1208	0.8491	0.05379
1529	2.2366	0.8979	0.05745
1530	2.2400	0.8997	0.05760
1532	2.1462	0.8629	0.05479
1536	2.0915	0.8476	0.05426
1537	2.0923	0.8478	0.05425
1538	2.0920	0.8478	0.05428
1539	2.0921	0.8475	0.05423
1541	2.0915	0.8473	0.05427
1542	2.0921	0.8476	0.05431
1543	2.1013	0.8480	0.05392
1544	2.1782	0.9134	0.05895
1545	2.0986	0.8481	0.05426
1546	2.0918	0.8477	0.05426
1550	2.1902	0.8842	0.05693
1551	2.1026	0.8468	0.05372
Other Materials			
*188	2.173	0.8929	0.05737
501	2.228	0.9615	0.06245
1317	2.1072	0.8500	0.05437
1547	2.0922	0.8478	0.05428
Some Japanese and Chinese Ores			
1548	2.0946	0.8460	0.05421
1549	2.1180	0.8566	0.05488
1800	2.1084	0.8473	0.05425
1801	2.0874	0.8443	0.05406
1802	2.0957	0.8449	0.05418
1804	2.0964	0.8463	0.05369
1805	2.0975	0.8490	0.05422

* Early data, less reliable.

TABLE 3

Samples Grouped by Isotope Ratios

VERY LOW RATIOS	
1009	Early Chinese
1005, 1006	Early Chinese, BaO
*	
1524	Early Chinese, BaO
MID-RANGE RATIOS	
†1007	Early Chinese, comp. unknown
**	
1008	Chinese glaze, late
**	
1800	Japanese ore
*	
1801	Japanese ore
*	
1802	Japanese ore
1548	Japanese ore
1804	Chinese ore
*	
1536, 1537, 1538, 1539	Shōsōin
1547	Red lead, Shōsōin
1541, 1542	Nara
1546	Japanese glaze, 10th–12th century
*	
†1551	Early Chinese, BaO
†1543	Chinese, 10th century
1545	Japanese, 19th century
†1805	Chinese ore
*	
1317	Japanese halberd, Pb metal, 3rd–4th century
MID-RANGE RATIOS	
**	
1549	Japanese ore
**	
†1528	Japanese, Kofun
**	
†1532	Japanese, Kofun
HIGH RATIOS	
1525	Yayoi, BaO
1550	Early Chinese (eye-bead), BaO
1521	Early Chinese, BaO
1520	Early Chinese, BaO
*(?)	
1523	Yayoi, BaO
1526	Yayoi, BaO
*(?)	
188	Chinese bronze, Chou
**	
†1529	Japanese, Kofun
†1530	Japanese, Kofun
**	
1527	Yayoi
**	
1544	Japanese, 12th century (?)
**	
†1522	Early Chinese, BaO
**	
501	Chinese white lead, late

Seligman, Beck, and Ritchie[13] first associated with the high-BaO composition. (See fig. 3) This is certainly encouraging and raises hopes that eventually it might be possible to identify a source (or a few possible sources) of manufacture for the early high-BaO glasses.

The picture quickly becomes complicated, however, by noting the results on nos. 1005/1006 (fig. 4) and no. 1524 (fig. 5) two other high PbO-high BaO glasses analyzed. The leads in these glasses are not only different, but are about as different as they could be, isotopically, from the other six high-BaO glasses. Whereas the first six fall in the highest

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[13] See Footnote 4.

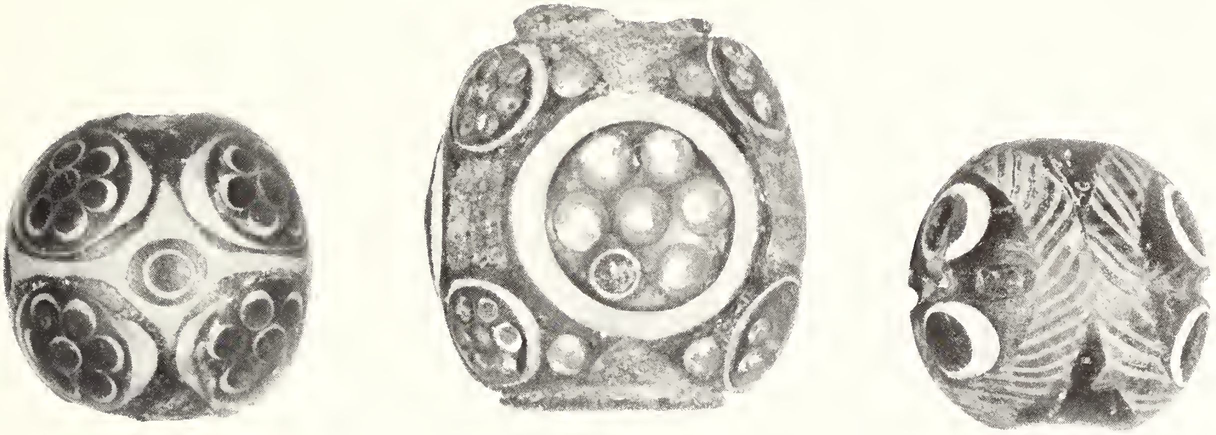

FIG. 3.—Group of Chinese beads of the type often containing high barium oxide. Sample 1550 is the bead on the right (CMG 51.6.549B). This bead contains $\simeq 24\%$ PbO and $\simeq 12.7\%$ BaO.

ranges of ratios we have yet found, these two fall close to the low limit in the lower left-hand corner of the graph. These are leads of entirely different geological age, and one is tempted to suppose that they came from a mine (or mines) distantly removed from the other mining region. There is, incidentally, nothing in the chemical analysis of no. 1524 which differentiates it from the other high-BaO glasses. (A complete chemical analysis has not yet been made of no. 1005.)

To make the picture somewhat more complicated, the nearest neighbor to nos. 1005 and 1524 is no. 1009 (fig. 6), another early glass of undoubted Chinese origin. This is a heavily-weathered glass *chape* or sword sheath terminal. Its lead could well have come from a mine near to that which supplied the lead found in no. 1005, but its chemical composition is quite different. This object, which also had a tentative Han date, is rich in lead but has only a minor concentration of barium

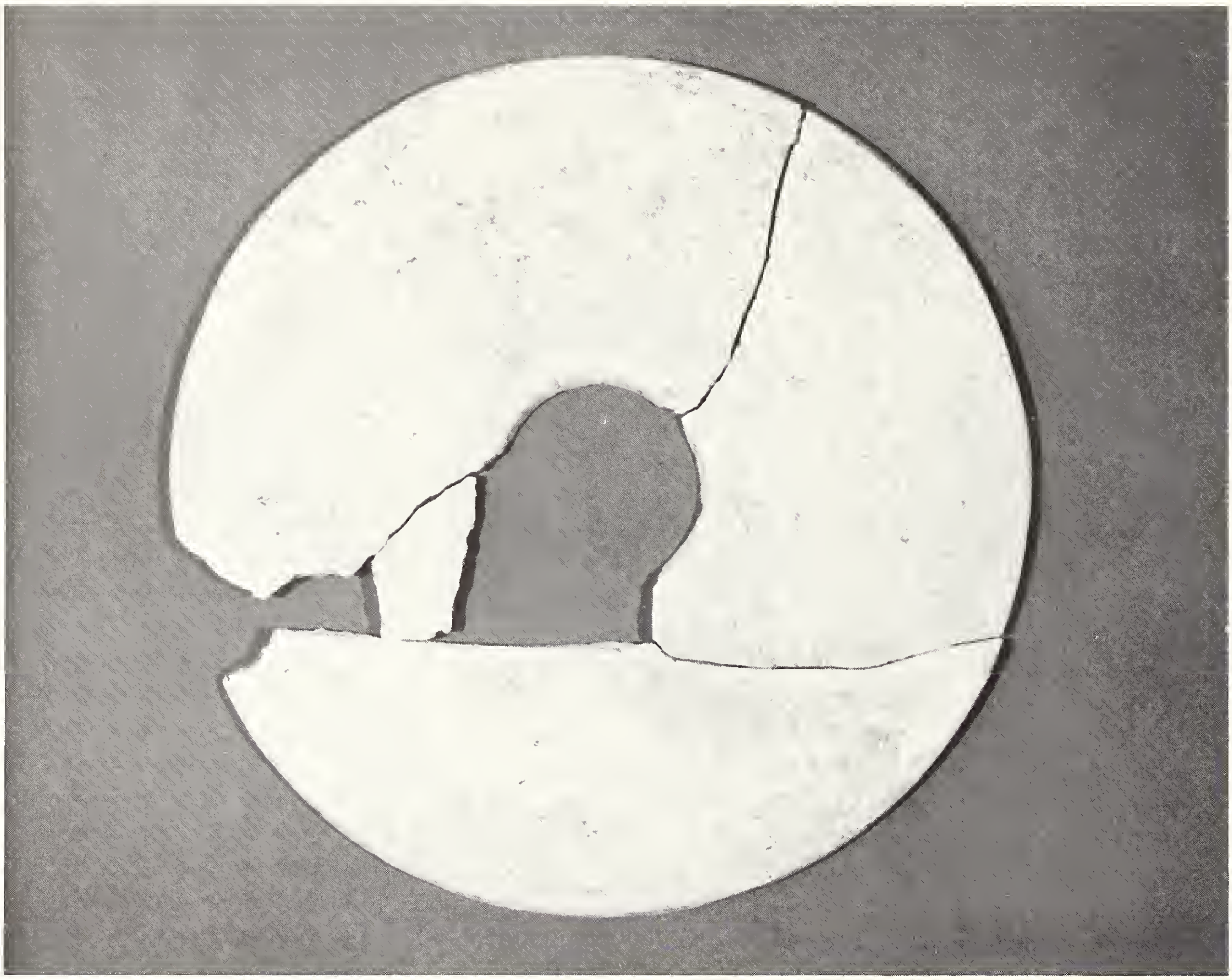

Fig. 4.—Chinese ritual *pi* disk. Sample 1005 is of the unaltered colorless glass; sample 1006 is of the weathering products (CMG 51.6.567). The weathering products contain $\simeq 37.9\%$ PbO and $\simeq 11.7\%$ BaO.

oxide (estimated at 0.4 percent in its weathering crust). It is of a different chemical type thought to be a bit later, but still known in Chinese glass.[14] Another Chinese *pi* disk, no. 1007, (not yet chemically analyzed) lies between the two extremes of high and low ratios. We can offer no explanation, except that its lead appears to have come from an entirely different source.

Three other glasses among the present samples bear probable or definite Chinese attributions. These are nos. 1522, 1527, and 1543. Nos. 1522 and 1527, the first excavated in Chin-ts'un near Lo-yang and the other in Fukuoka Prefecture, fall in the upper right-hand part of Figure 1. They are in the same general part of the graph as the cluster of six high-BaO Chinese glasses but differ significantly from them. No. 1527 resembles two other somewhat later glasses discussed below

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[14] See Footnote 4.

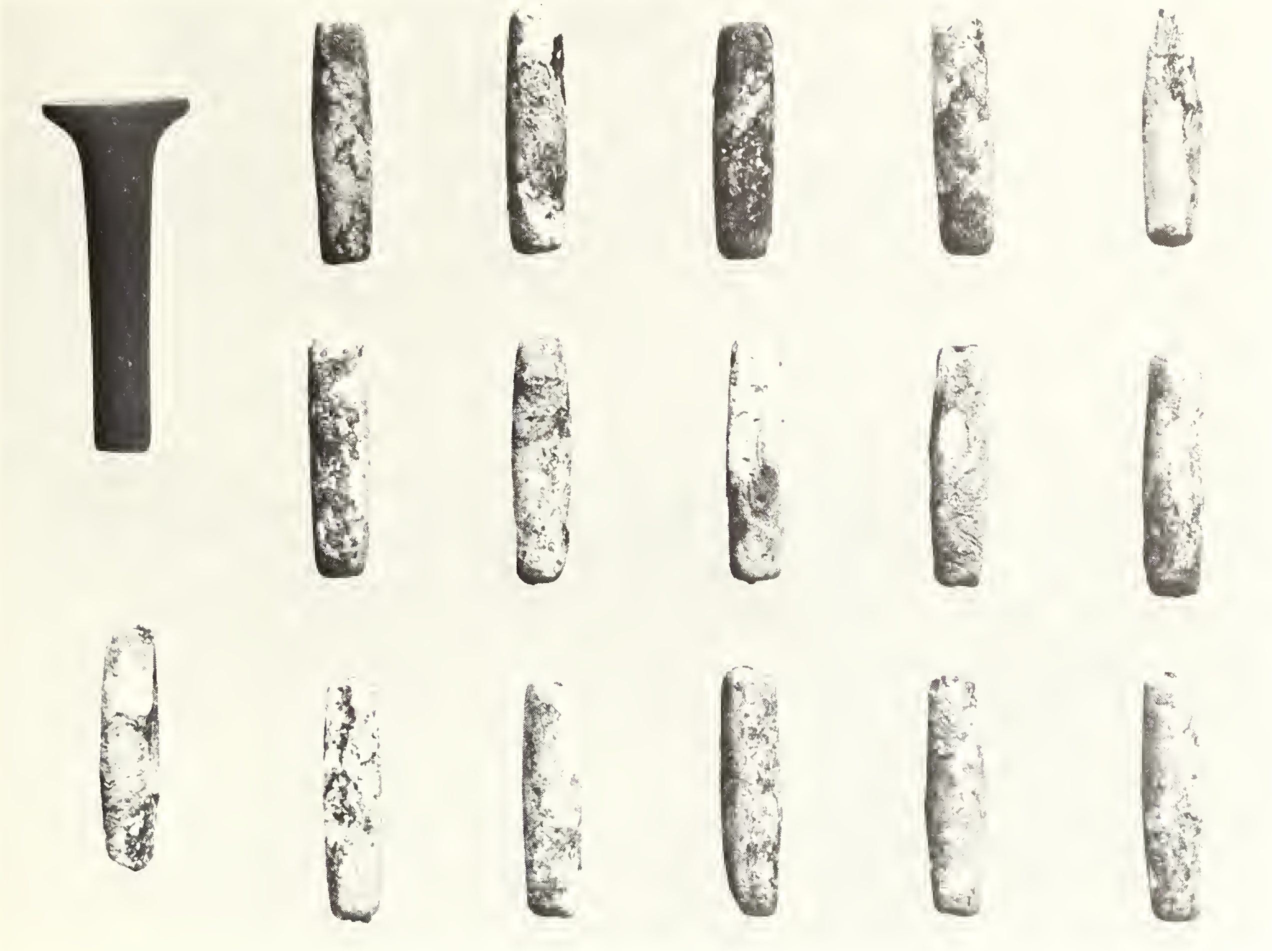

FIG. 5.—Group of tubular beads and a pestle-like bead excavated in pottery coffin at Sugu-Okamoto, Fukuoka Prefecture. × 1.6. Same as Plate 1 in: Sueji Umehara, *Nihon Jōko no Hari* (Ancient Glasses in Japan) *Shirin*, vol. 43 (1960), p. 1. Courtesy of S. Umehara. Sample 1524 excavated in Tateiwa is similar in shape to the pestle-like rod rod in the upper left corner but is heavily weathered.

(nos. 1529 and 1530). No. 1525, which is completely weathered with no glass remaining, contains only a trace of BaO. However, the original glass might have had high BaO judging from the shapes and sizes of beads excavated in similar coffins. No. 1527 is rich in lead but is without BaO. No. 1543, which was brought to Japan in 987 A.D. but which could have been made sometime earlier in China, falls between those samples we have been discussing; it is shown more clearly on Figure 2.

In the upper right-hand part of Figure 1 near the cluster of high-BaO glasses are some other glasses. These are nos. 1529 and 1530, two glasses excavated in Fukuoka Prefecture and dating from the Late Kofun Period (ca. sixth to seventh century A.D.), and another glass of uncertain, but seemingly later date, no. 1544 from Shimane Prefecture. Nos. 1529

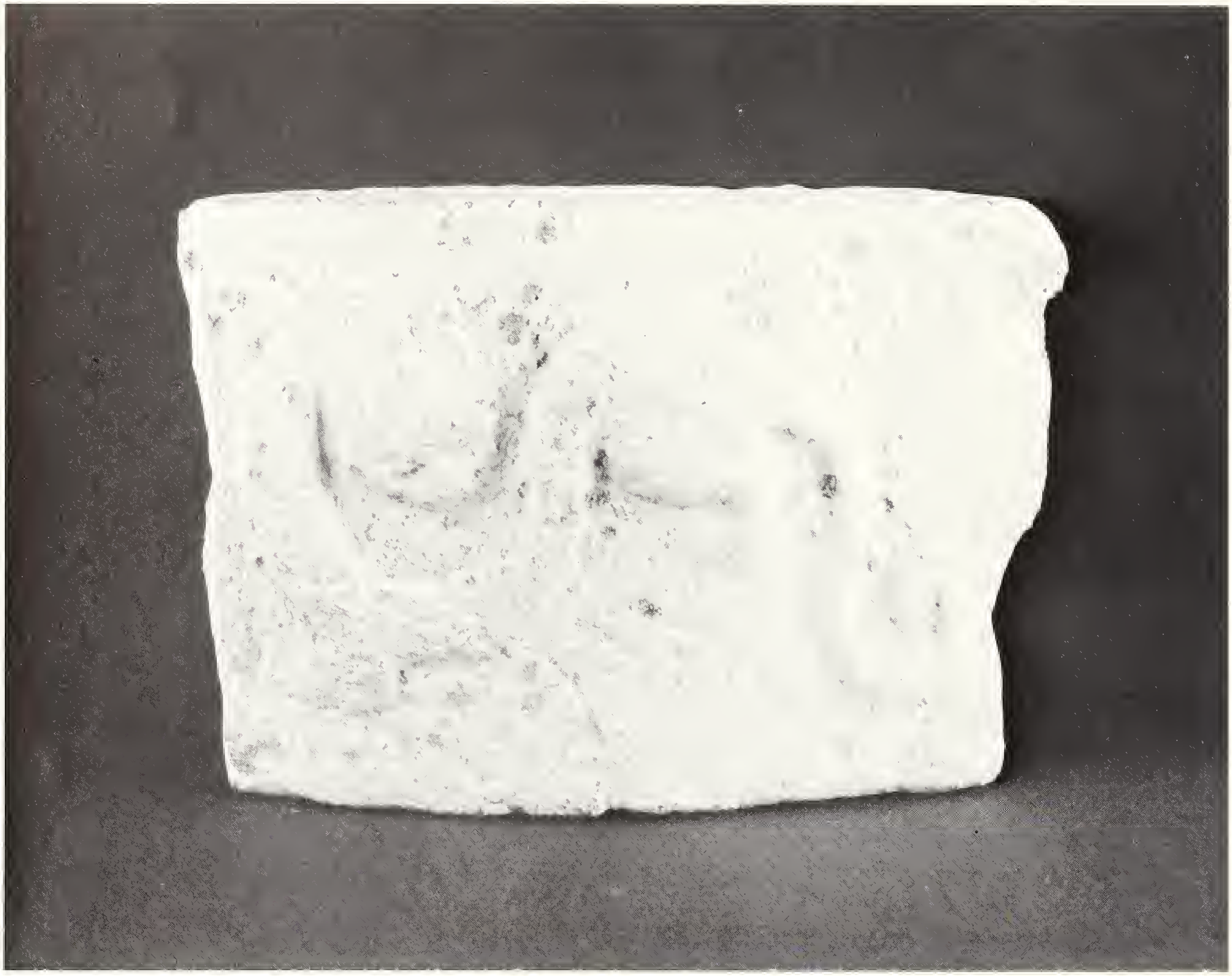

FIG. 6.—Chinese sword sheath terminal of heavily-weathered colorless glass; thought to date from the Han Dynasty. Sample 1009 is of the weathering products (CMG 62.6.15). The weathering products contain $\simeq 25\%$ PbO, but only $\simeq 0.4\%$ BaO.

and 1530 are very similar and lie on the upper trend, along with glass bracelet no. 1527 mentioned above, which might indicate that they too are of Chinese origin. However, no. 1528, another bead from the same site as these two Kofun Period beads (nos. 1529 and 1530) falls near the center of the graph. It is markedly different from its two companions. No. 1532 is still another bead of the Kofun Period, but it comes from a different site. Its ratios fall between the other Kofun Period beads, along the upper linear trend.

One further observation on the Chinese glasses should be made. Nos. 1005 and 1006 are from the same object. One is of the weathering product of the glass, and the other of the unaltered glass itself. The data for these two samples agree very well with one another, the difference between them being within the experimental error for the procedures used.

This confirms that in this case (as is expected to be the general rule), the processes of chemical decomposition have no measurable fractionation effects upon the lead isotope ratios.

Towards the middle range of Figure 1 and illustrated more clearly in Figure 2 is a group of samples of very great importance. These include four samples of glass (and one of a red lead pigment) from the Shōsōin repository in Nara. These glasses of the eighth century are part of the marvelous treasures preserved in that sacred place. The isotopic compositions of the leads in these samples (nos. 1536, 1537, 1538, 1539, and 1547) are identical, within even the high accuracy of the method used to determine them. They must have come from the same galena deposit. Two other glasses from Nara, from the Yakushiji Temple (nos. 1541 and 1542), are indistinguishable from the Shōsōin samples. These date from the first half of the eighth century A.D. All are joined by an eighth sample (no. 1546), which is from a ceramic glaze found at a kiln site in Komaki city, Aichi Prefecture, near Nagoya. This bears no archaeological similarity to the Nara glasses and dates from the 12th century A.D., but it appears to contain lead from either the same mine or one very much like it.

We have included in Figures 1 and 2 data for five Japanese galena ores. While it is not an exact match for the Nara-type leads, no. 1548, an ore from the Budō mine in Niigata Prefecture, is quite close. Had we not been spoiled by the extraordinarily close fit of the eight samples within that cluster—which are literally indistinguishable—the ore no. 1548 might have been judged as a reasonable match for the Nara group. Three other Japanese ores analyzed at the National Bureau of Standards resemble the Nara-type lead as closely as does no. 1548. In fact, the four ores when plotted almost bracket the Nara leads on the graph. The four are: no. 1802, from a mine in the village of Shimo-Tsugu, Aichi Prefecture; no. 1548, from the Budō mine, further to the northeast in Niigata Prefecture; no. 1801, from the Arakawa mine in Akita Prefecture, well to the north; and no. 1800 from the Kuratani mine, Kanazawa city along the Japan Sea coast. These four ores are quite similar to one another on the graph, but their sources are dispersed geographically, being strung out along the island of Honshu. Another Japanese ore, no. 1549 from the Kamioka mine in Gifu Prefecture in Central Japan differs somewhat from the other four in its isotopic composition.

This whole discussion illustrates that geographical proximity does not necessarily imply isotopic identity and that isotopic similarity does not imply close geographical proximity. Overall, however, the isotopic variability among the Japanese ores we have analyzed so far is not so great as to be discouraging, but not so small that it will prevent one from distinguishing among galenas from different regions within Japan.

In a recent paper, Prof. M. Murozumi and one of the authors (KY) reported lead isotope data for some Chinese and Japanese bronzes, mostly mirrors, along with early data on some Japanese ores.[15] We have not plotted these ore data individually here, because it is not known if the early experimental results are in calibration with those of the National Bureau of Standards. However, these early data, when plotted as a group, also include the Nara type of lead found in the glasses. Thus, there is good reason to believe that the source of lead which found its way into the Nara glasses will be narrowed down to a few possibilities and may possibly be uniquely identified in the future. We should add that from these findings, there can be but little doubt that the Nara glasses were made in Japan.

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[15] K. Yamasaki and M. Murozumi, "An Attempt to Determine the Sources of Archaeological Relics by Lead-Isotope Ratio Determination," presented at a symposium at Nara, Jan. 28, 1977. See also Footnote 2. For earlier data on Japanese ores see: H. Sakai *et al.*, *Bulletin of the Chemical Society of Japan*, 28 (1955), p. 533; *Geochimica et Cosmochimica Acta*, 15 (1958) p. 1; and Sato *et al.*, *Geochemical Journal*, 7 (1973), p. 115. More recent data on Japanese galena ores and Chinese and Japanese bronze objects have been published in, K. Yamasaki, M. Murozumi, S. Nakamura, M. Hinata and M. Yuasa, *Nippon Kagaku Zasshi* (J. Chem. Soc. Japan, Chemistry and Chemical Industry), 1978, (8), 1112–1117.

An interesting cluster of four additional samples lies just above the Nara leads. These include a large, heavily-leaded blue glass bead with a high barium oxide content thought to be Chinese (no. 1551), a fragment of a glass bottle brought from China to Japan in 987 A.D. (no. 1543 mentioned above), a 19th century glass from Nagasaki (no. 1545), and metallic lead from a third to fourth century halberd excavated in Karatsu, Saga Prefecture (no. 1317). On the basis of the plot in Figures 1 and 2, the four samples all look quite a bit alike. However, when plotted on a graph of the Pb^{204}/Pb^{206} vs. Pb^{207}/Pb^{206} ratios (not illustrated), they do not agree very well. Two of them (nos. 1317 and 1545) resemble one another and fall close to the Nara leads and known Japanese ores, while the other two (nos. 1543 and 1551) are different and do not fall close to the Nara group. Although there is still room for debate, it appears that the lead in the halberd (no. 1317), like that in the late Nagasaki glass (no. 1545), probably came from Japan, whereas the two glass objects (nos. 1543 and 1551) are of Chinese origin, as suspected. It might be noted in passing that the two glasses, just judged to be Chinese, resemble very closely a lead-containing ore from Kwangtung Province (no. 1804) on both graphs of the data. Moreover, the acceptance of these glasses as having Chinese origins also illustrates that it would be simplistic to assume that all Chinese leads must lie along the upper trend of the Pb^{208}/Pb^{206} vs. Pb^{207}/Pb^{206} plot, because these, at least, do not.

No. 1008 is from the bright-yellow opaque glaze on an 18th century Imperial Yellow Chinese ceramic. The object, in the collection of Dr. E. T. Hall, was made in Ching-te-chen. The point falls in the central part of Figure 1 and does not bear a close relationship to any of the other samples run, although it does resemble one of the Chinese bronzes. Finally, no. 501, a Chinese white lead pigment presumably of quite recent date, falls far off to the right.

CHINESE GALENA ORES

We have begun a search for information on lead mines in China and the history of early Chinese mining, but at present have not turned up a significant amount of what we regard as reliable information. A few specimens of Chinese (and Japanese) ores have been run at the National Bureau of Standards, and are shown on Figures 1 and 2 with abbreviated descriptions. Table 4 indicates possible locations of lead, lead-zinc, or "silver" deposits in China. If nothing more, these data show wide-spread occurrence of lead ores and suggest that a considerable variation in isotope ratios should be expected to exist among them. Many more samples and determinations will be necessary before we will begin to have a definitive idea of lead isotopes in Chinese galenas.

TABLE 4
Chinese Lead Ores

Province	Locality
Anhwei	T'ung-ling
Chekiang(?)	—
Fukien(?)	—
Honan	*Chin-ts'un (near Lo-yang)
	*Hsin-cheng (near Cheng-chou)
Hopeh	Ku-shan-tze Yan-shu-lin } (near Ch'eng-te)
Hunan	Shui-k'ou-shan (no. 1805)
	*Ch'ang-sha (no. 1520)
Kiangsi	Ching-te Chen[†]
Kwangsi	—
Kwantung	—(no. 1804)
Kweichow	—
Liaoning	Shen-yang (West of Tan-tung)
Shantung	—
Szechwan	Hui-li
Yunnan	Shih-p'ing

* Archaeological sites where high-BaO glasses have been excavated. Lead deposits may or may not occur nearby.

[†] No. 1008 is from here.

SUMMARY

This research has demonstrated that lead isotope data are useful for the classification of East Asiatic glasses. A clearly-defined Nara type of lead has emerged, based upon the findings for the Shōsōin glasses and a few others from Nara. This type falls within the rather restricted range of lead isotope ratios of Japanese ores so far analyzed, but probably is not unique to Japan. Other glasses excavated in Japan contain leads which differ considerably from the Nara type. Some of these were believed beforehand to be of Chinese origin on the basis of archaeological information, and this was borne out by the lead isotope findings. Isotope ratios of two markedly different types were found in early Chinese glasses. These leads generally lie near the extremes of the overall range of lead isotope ratios we have determined through the years, but a few fall in an intermediate range. While tight clustering of Chinese glasses was found in some instances, there was only a partial correlation between the lead isotope data and the chemical composition of the glasses as characterized by barium oxide contents. The wide spread of isotope data for the Chinese glasses must reflect a correspondingly wide variation in geological ages among galenas occurring in China. A continuation of these studies should certainly prove worthwhile, particularly as our knowledge of ores from China improves, and we welcome the submission of specimens suitable for study from all interested persons.

ACKNOWLEDGMENTS

The authors express their thanks to the many individuals who have assisted in various ways in this research and in the preparation of the publication. They are grateful to those in Japan who provided the glass samples used for this research, especially to Dr. Sueji Umehara, Professor Emeritus of Archaeology, Kyoto University. Dr. C. Iida, Mr. T. Tanaka, and Miss T. Murase in Nagoya University helped in the spectrographic and chemical analyses. Many people at the National Bureau of Standards helped in the preparation of the samples and the mass spectrometry. At The Corning Museum of Glass, Mrs. Judy Snyder helped in the recording and collating of data, in the compilation of the catalogue, and in the preparation of the manuscript. We thank

Mr. W. T. Chase of the Freer Gallery for permission to discuss data on the Chinese bronzes, Miss Dorothy Blair of Corning for her advice on dating the glasses, Mr. Paul E. Desautels of the National Museum of Natural History who provided several ore samples, and Mr. John E. Dayton of London who provided ore sample no. 1804. The densities of the glass were determined by Mr. John F. Wosinski and his co-workers in Corning Glass Works, and the X-ray fluorescence analyses for PbO and BaO were run by Mrs. Janice Carlson and Mr. Victor Hanson of the Henry Francis du Pont Winterthur Museum. Mr. Nicholas Williams of The Corning Museum of Glass photographed the glasses illustrated. Mr. Jerome Smith of the Lead Industries Association, Inc. and Mr. Martin S. White of the Zinc/Lead Library and Abstracts both provided some references in our search for information on Chinese ores.

CATALOGUE OF SAMPLES

JAPANESE AND CHINESE GLASSES

1005 Chinese ritual *pi* disk of glass. Colorless, heavily weathered. Sample is of unweathered glass. CMG 51.6.567; Chem. anal. no. 3330.

1006 Weathering product of no. 1005. CMG 51.6.567; Chem. anal. no. 3331. PbO $\simeq$ 38%; BaO $\simeq$ 11.7%. (X-ray fluorescence, Winterthur Museum).

1007 Chinese ritual *pi* disk of glass. Green turbid color, slight weathering. Sample is of unweathered glass. CMG 51.6.548.

1008 Glaze from a fragment of Imperial Yellow Chinese ceramic. Made at Ching-te-chen. 18th century. From collection of E. T. Hall, via R. E. M. Hedges at Oxford University. PbO $\simeq$ 30%. (Emission spectrography, CMG)

1009 Fragment of Chinese "carved" glass sword terminal. Thought to be Han Dynasty (206 B.C.–220 A.D.). Slightly turbid, colorless, some white powdery corrosion products. Sample is of unweathered glass. CMG 62.6.15; Chem. anal. no. 3329. PbO $\simeq$ 25%; BaO $\simeq$ 0.4%. (Emission spectrography, CMG)

1520 Chinese ritual *pi* disk of glass. Excavated in Changsha, Hunan. Warring States Period. Dark green color, heavily corroded. Donated by S. Umehara. Same as no. 4, table 1 in: K. Yamasaki, "Chemical Compositions of Ancient Glasses Found in Japan," *Proceedings of the Tenth International Congress on Glass* (Kyoto: The Ceramic Society of Japan, 1974), no. 9, pp. 15–20. PbO $\simeq$ 46.1%; BaO $\simeq$ 14%; apparent density 4.0.

1521 Chinese ritual *pi* disk of glass. Warring States Period. From the Eguchi Collection. Dark green color, heavily corroded. Donated by S. Umehara. Same as no. 3, table 1 in: Yamasaki, "Chemical Compositions . . ." PbO $\simeq$ 48.5%; BaO $\simeq$ 13%; apparent density 4.3.

1522 Corrosion product of glass eye-bead. Excavated in Chin-ts'un, Lo-yang, China. Donated by S. Umehara. BaO detected by qualitative spectrographic analysis.

1523 Cylindrical, tubular glass bead. Excavated at Sugu-Okamoto, in a pottery coffin, Kasuga city near Fukuoka city, Fukuoka Prefecture. First century B.C. Length: ca. 2 cm. Diam.: 5 mm. Dark green color, heavily corroded. Donated by S. Umehara. Same as no. 1, table 1 in: Yamasaki, "Chemical Compositions . . ." PbO $\simeq$ 38.5%; BaO $\simeq$ 14%; apparent density 3.8.

1524 Rod or pestle-shaped glass. Excavated at Tateiwa, in pottery coffin no. 28, Iizuka city, Fukuoka Prefecture. Yayoi Period. Length: ca. 3 cm. Width: 1.5 cm. Dark green color, heavily corroded. Reference: Tateiwa Iseki Chōsa Iinkai (Archaeological Research Commission for Tateiwa). *Tateiwa Iseki* (Tateiwa). (Tokyo: Kawade Shobō, 1977) Same as no. 2, table 1 in: Yamasaki, "Chemical Compositions . . ." PbO $\simeq$ 40.8%; BaO $\simeq$ 16%.

1525 Corrosion product of tubular glass bead in which no unaltered glass remained. Excavated at Tateiwa, in the same pottery coffin as no. 1524, Iizuka city, Fukuoka Prefecture. X-ray diffraction revealed the main constituent to be lead phosphate.

1526 Cylindrical, tubular glass bead. Excavated at Uki-Kunden, in pottery coffin no. 10, Karatsu city, Saga Prefecture. Yayoi Period. Length: 8 mm. Width: 7 mm. Dark green color, heavily corroded. Donated by T. Okazaki. Apparent density 3.8.

1527 Fragment of glass bracelet. Fukuoka Prefecture. Yayoi Period. Heavily corroded. Donated by S. Umehara.

1528 Round glass bead. Found at back of Miyajidake shrine, in a tomb, Fukuoka Prefecture. Kofun Period. Height: 9 mm. Width: 7 mm. Dark green color, corroded. Donated by S. Umehara. Same as no. 9a, table 2 in: Yamasaki, "Chemical Compositions . . ." PbO $\simeq$ 71.2%; apparent density 4.9.

1529 Round glass bead similar to no. 1528. Found at back of Miyajidake shrine, in a tomb, Fukuoka Prefecture. Kofun Period. Dark green color. Donated by S. Umehara. Same as no. 9b, table 2 in: Yamasaki, "Chemical Compositions . . ." PbO $\simeq$ 75.6%; apparent density 5.4.

1530 Fragment of flat glass plate. Found at back of Miyajidake shrine, in a tomb, Fukuoka Prefecture. Kofun Period. Dark green color, corroded. Donated by S. Umehara. Same as no. 9c, table 2 in: Yamasaki, "Chemical Compositions . . ." PbO $\simeq$ 74.0%; apparent density 5.3.

1532 Round glass bead. Excavated from the Takakura tomb, Nagoya city. Kofun Period. Height: ca. 11 mm. Dark green color, corroded. Donated by S. Narasaki. Same as no. 8, table 2 in: Yamasaki, "Chemical Compositions . . ." PbO ≃73.9%; apparent density 4.7.

1536 Fragment of round glass bead. Preserved in the Shōsōin repository, Nara. Height: 8 mm. Width: 9 mm. (A Shōsōin bead which had been analyzed in 1959–1961.) Brown color. Reference: Shōsōin Office (Editor). (*Shōsōin no Garasu* (Glass objects in Shōsōin (Tokyo: Nihon Keizai Shinbun, 1965). Same as no. 12, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃72.6%; apparent density 5.3.

1537 Round glass bead similar to no. 1536. Preserved in the Shōsōin repository, Nara. Reddish-brown color. Reference: see no. 1536. Same as no. 13, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃73.6%; apparent density 5.3.

1538 Round glass bead similar to no. 1536. Preserved in the Shōsōin repository, Nara. Dark green color. Reference: see no. 1536. Same as no. 14, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃71.9%; apparent density 5.3.

1539 Round glass bead. Preserved in the Shōsōin repository, Nara. Height: 5 mm. Width: 6 mm. White opaque bead opacified with excess insoluble silica. Reference: see no. 1536. Same as no. 15, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃66.0; apparent density 4.4.

1541 Fragment of round glass bead. Found in Yakushiji Temple, inside pedestal of main Buddha of the Golden Hall, Nara. 710–794 A.D. Dark green color. Donated by S. Umehara. Reference: Yakushiji Shūri Iinkai (Repair Committee for Yakushiji), *Yakushiji Kokuhō Yakushi Sanzon tō Shūri Kōji Hōkokusho* (Report on the repair works of Yakushi three figures, national treasure in Yakushiji) (Tokyo, 1958) Same as no. 10, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃70%; apparent density 5.3.

1542 Round glass bead similar to no. 1541. Found in Yakushiji Temple, inside pedestal of main Buddha of the Golden Hall, Nara. Yellow color. Reference: see no. 1541. Same as no. 11, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃66%; apparent density 5.1.

1543 Fragment of small Chinese glass bottle for Buddha's bone. Found in Seiryōji Temple, inside image of Sakyamuni, Saga, Kyoto. Documentary evidences show that the image was made in 985 A.D. and brought to Japan in 987 A.D. Bluish-violet color. Donated by S. Umehara. Reference: Tsuneo Yoshimizu. *Seiryōji Shaka Nyorai Ryūzō no Tainai Nōnyū Butsu no Garasu ni tsuite* (On the glass objects incorporated inside the Sakyamuni image of the Seiryōji Temple). *Waseda Bijutsushi Kenkyū* (The study of the history of art, Waseda University), no. 4 (1966), pp. 53–72. Same as no. 17, table 3 in: Yamasaki, "Chemical Compositions . . ." PbO ≃55.8%. (Note: Yoshimizu supposes from the technological point of view that these bottles were made in a local factory near a port, Linhai, in Chekiang, where the priests sailed for Japan bringing the image in question.)

1544 Glass lump. Excavated at Tamayu Village, Shimane Prefecture. Supposed date 12th century. Now preserved in the Kyoto National Museum. Dark bluish-green color.

1545 Fragment of glass bamboo pole. A decoration attached to the *Kasaboko*, a Japanese umbrella-like float shown to the public on the occasion of the festival of Suwa shrine, Nagasaki city, owned by the Imauo-cho, Nagasaki city. Edo Period (probably mid-19th century). Bluish-green color. Donated by E. Esaki. For the festival of the Suwa shrine and the floats dedicated to the shrine see: D. Blair, *A History of Glass in Japan* (Tokyo: Kodansha International and The Corning Museum of Glass, 1973), p. 400.

1546 Lead glaze from pottery sherd. Excavated at Komaki city, Shinooka kiln no. 5, Aichi Prefecture. Date 10th–12th century. Dark green color. Donated by S. Narasaki. Reference: K. Yamasaki. *Honpō shutsudo no Saiyū Tōki no Uwagusuri oyobi Taido no Kagakuteki Kenkyu* (Chemical studies on the glazes and bodies of the color-glazed potteries found in Japan), *Tōyō Tōji* (Oriental Ceramic), vol. 2 (1973/1974), pp. 55–63.

1550 Fragment of Chinese glass eye-bead. May be from Lo-yang (possibly the village of Chin-ts'un). Dark blue, transparent, moderately weathered. CMG 51.6.549B. Similar to beads illustrated in: C. G. Seligman and H. C. Beck, "Far Eastern Glass: Some Western Origins." *Bulletin of the Museum of Far Eastern Antiquities* (Stockholm), no. 10 (1938) pp. 1–64, plates IV and V. PbO $\simeq 24\%$; BaO $\simeq 12.7\%$; (X-ray fluorescence, Winterthur Museum) Apparent density 2.95.

1551 Large Chinese glass bead. Uncertain provenance, thought to be Chinese. Probably early. Blue color, heavily weathered. Same as CMG 67.6.2. PbO $\simeq 39.3\%$; BaO $\simeq 8.6\%$; X-ray fluorescence, Winterthur Museum. Apparent density 3.84.

OTHER MATERIALS

188 Small sample of lead chloride recovered from the analysis of the swing handle of a Chinese bronze ceremonial vessel type *yu*, FGA 30.26, dating from the early Chou dynasty, 11th cent. B.C. The alloy contains 11.6% Pb. Rutherford J. Gettens, Freer Gallery of Art. This lead was found to be entirely different from the leads found in any of the other archaeological objects studied. It was probably derived from an ore of Precambrian Age. Precambrian rocks are widespread in China. (Note: This entry was copied from original publication of no. 188 in: R. H. Brill and J. M. Wampler, "Isotope Studies of Ancient Lead," *American Journal of Archaeology*, vol. 71 (Jan. 1967), p. 76.

501 Chinese white lead pigment. Collected in 1925, Lan-Chou-Pu, Kansu. From the E. W. Forbes Collection at the Fogg Museum. Sample provided by Dr. R. Feller, who assigned it no. F2217. Reference: R. H. Brill, W. R. Shields, and J. M. Wampler, "New Directions in Lead Isotope Research," *Application of Science in Examination of Works of Art* (Boston: Museum of Fine Arts, 1970), pp. 73–83.

1317 Metallic lead halberd. Excavated in tomb, Karatsu, Saga Prefecture, Kyushu. Third to fourth century. (Chinese or Japanese.) Origin was not known.

1547 Powdered red lead pigment of the "superior" quality. Preserved in the Shōsōin repository, Nara. Eighth century. Yellowish-red color. Reference: K. Yamasaki, "Chemical studies on the Eighth-Century Red Lead Preserved in the Shōsōin at Nara," *Studies in Conservation*, vol. 4 (1959), pp. 1–4; also, K. Yamasaki, "*Entan* (Red Lead)," *Shōsōin Medicinals*, ed. Y. Asahina (Osaka, 1955).

SOME JAPANESE AND CHINESE ORES

1548 Galena; Būdo mine, Iwafune County, Niigata Prefecture.

1549 Galena; Kamioka mine, Gifu Prefecture. This mine has galena of different geological ages.

1800 Galena with baryte, arsenopyrite, and sphalerite, Kuratani mine, Kanazawa city, Ishikawa Prefecture, Japan (R479).

1801 Galena; Arakawa mine, Akita Prefecture, Japan (R8450).

1802 Galena with stibnite; mine at Shimo-Tsugu village, Kita-Shidara County, Aichi Prefecture, Japan (108475).

1804 Bournonite; Kwangtung Province, China (90614).

1805 Galena; Shih-k'ou'shan, Hunan Province. Specimen provided by Mr. John E. Dayton of London.

NOTE: Nine samples of galena ores from the collection of the National Museum of Natural History in Washington, D.C. were provided by Mr. Paul E. Desautels, but they have not yet been analyzed.

THE PROVENANCE OF EARLY ISLAMIC LUSTRE WARES

By JAY D. FRIERMAN*
FRANK ASARO†
AND HELEN V. MICHEL†

Glazed ceramics decorated with overglazed lustre painting first appeared in the ninth century in the Near East. From their beginning they seem fully developed, and among the earliest found are the very sophisticated polychrome lustres in which a variety of lustre and non-lustrous glazes are combined on a single vessel. This is a technical *tour de force* that indicates a long experience with this difficult process. The generally accepted assumption is that lustre decoration on earthenwares grew out of lustre glass painting which has a history beginning in the fourth or fifth century A.D. in the Near East and which was in a fully developed state before the eighth century.[1]

Lustre wares were very widely dispersed and in rather impressive quantities. Such extensive trading patterns were not unusual. It has been shown at Siraf for example, that the enormous trade in fine "Samarra" wares was at least equalled by trade in blue-green common wares.[2] The polychrome lustres appear in the first half of the ninth century in Iraq and are abandoned towards the end of that century in favor of the technically less demanding monochrome lustres.[3] At some point in the eleventh century, faience[4] bodies begin to replace earthenware as the base for lustre decoration. However, for special purposes, lustre on tin-opacified lead glazed earthenware bodies continued; the famous Kashan tiles of the thirteenth century are an example.

In the present work, neutron activation analyses on a limited sampling of sherds result in a number of suggestions which could be evaluated by measurements on a large sampling. These possibilities are: that the earthenware lustres of the ninth and tenth centuries may have been made in Iraq, *wherever excavated*; that in the eleventh century the technique of lustre painting was introduced into Egypt; and that by the end of the twelfth century it was being used in Egypt, Syria, Iraq, and Iran. The work also suggests that the innovation which caused lustre painting on glass to be used on glazed ceramics took place in Mesopotamia. The archaeological data presently available to support this latter contention, however, are modest.

THE PROCESS

Lustre painting is an overglaze technique of considerable technical sophistication which can be applied to either glazed faience or

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[1] A. Lane, *Early Islamic Pottery* (London: Faber and Faber, 1965) p. 14. R. H. Brill, "Chemical Studies of Islamic Luster Glass," in R. Berger, ed., *Scientific Methods in Medieval Archaeology* (Berkeley: University of California, 1970), pp. 351–377.

[2] D. Whitehouse, "Neutron Activation and the Provenance of Islamic Pottery from the Persian Gulf." Paper read at Conference on the Applications of the Physical Sciences to Medieval Ceramics, March 18–22, 1975.

[3] Lane, *Early Islamic Pottery*, pp. 14–15.

[4] Faience in this context refers to any of a variety of synthetic ceramic bodies consisting of ca. 80% silica, 10% clay and 10% frit or alkaline flux.

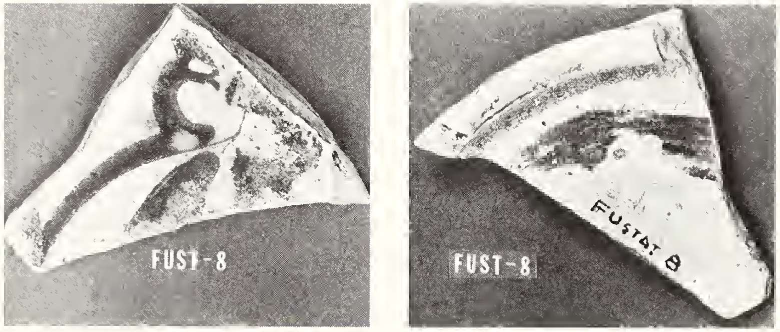

Fig. 1.—FUST-8, 9th century polychrome lustre earthenware, interior, exterior.

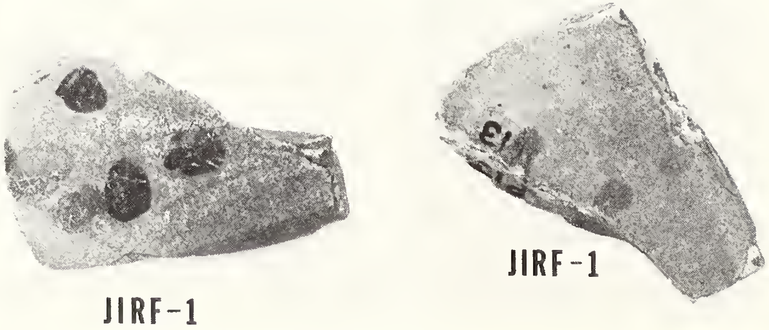

Fig. 2.—JIRF-1, 9th century polychrome lustre earthenware, interior, exterior.

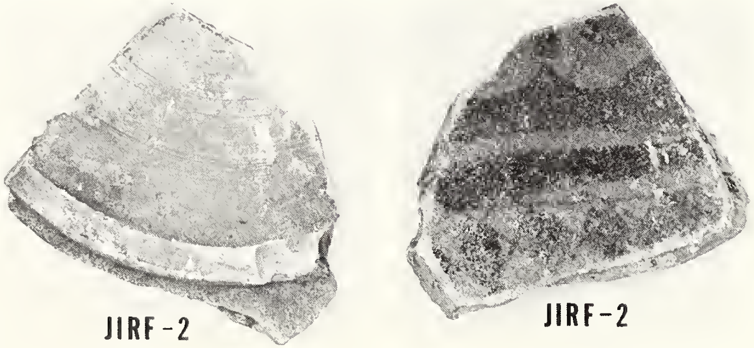

Fig. 3.—JIRF-2, 9th century polychrome lustre earthenware exterior, interior.

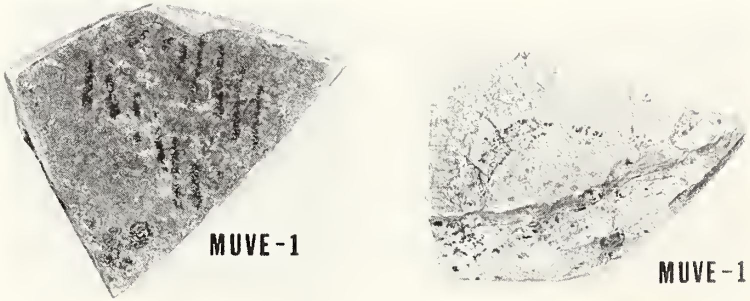

Fig. 4.—MUVE-1, 9th century polychrome lustre earthenware, interior, exterior.

glazed earthenware.[5] The normal practice seems to have been to first fire the unglazed body. In the case of faience, where underglaze decoration is employed, the pigment colorants are next applied and the fired pots are then glazed; if they are earthenware—usually a white tin-opacified lead glaze is used, and if faience—either a transparent or an opacified glaze. In either case a slip is unnecessary, because the tin-lead glaze is opaque and the faience body is generally pure white. This is followed by a second firing after which the pots are ready for the application of the lustre paint. The final firing was in a kiln reserved for this purpose, having a reducing atmosphere, and a temperature below that required to make the glaze fluid.

Lustre paint has been described as a mixture of natural and artificially produced oxides and sulfur compounds of copper, silver, iron, and arsenic, which were finely ground and mixed with either vinegar or grape juice.[6] In the reducing atmosphere of the lustre firing kiln, the copper would be reduced to the metallic state suspended in colloidal form in the glassy surface of the glaze, and would appear to the eye as a reflecting metal film.

THE PROBLEM

There has been much speculation on the place of manufacture of the early Islamic lustre wares. These speculations are based on the only methods of provenance determination previously available—stylistic studies and historical data. Lane felt that Iraq was the source and Baghdad the likely place of manufacture, but adds that, ". . . the point at which lustre-painting on pottery began in Egypt cannot be determined by literary or historical records".[7] Kühnel had originally shared this view, but in later years he believed that the process was introduced into Egypt before the end of the ninth century.[8] Schnyder in his definitive article fully discusses these opinions.[9] He also supported the early introduction of lustre manufacturing into Egypt.

The problem has been compounded by the wide use of samples of unknown provenance, the small number of medieval Near Eastern sites which have been carefully excavated and reported, and the lack of published kiln wasters or other definitive data from many of the most important sites. To these problems must be added the enormous amount of trade in ceramics which we see throughout the Early Islamic world.[10] In most large sites we are confronted with a bewildering array of indigenous styles, imports, and locally-made imitations.

METHOD

In recent years, neutron activation analysis has offered us analytical techniques which can be of great usefulness in the objective determination of the provenance of ceramics.[11] A small sample (100 milligrams) is removed from the cleaned body of the sherd with a synthetic sapphire drill; the powder is mixed with cellulose binder and pressed into a pill of uniform size. The sample pills together with pills of a "Standard Pottery" whose chemical composition is precisely known are then placed in a nuclear reactor and irradiated with neutrons. This causes the chemical elements in the samples to become radioactive and to emit gamma rays that have characteristic energies, and which decay with characteristic half-lives. The energy of the emitted gamma rays identifies the specific chemical element, and by measuring the intensity of the gamma ray in the standard pottery and the sample, approximately 40 elements may be quantitatively determined. The radioactive samples are analyzed with germanium gamma-ray spectrometers at five different times selected to achieve the best data for nuclides with a variety of half-lives from a few minutes to several years in length. In practice, 18 to 20 elements are used to establish a chemical "fingerprint".

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[5] J. W. Allan, "Abū'l-Qāsim's Treatise on Ceramics," *Iran*, vol. 11 (1973), pp. 111–120.

[6] Ibid, p. 114, §27. Brill, "Chemical Studies," p. 377. Hans E. Wulff, *The Traditional Crafts of Persia* (Cambridge: Massachusetts Institute of Technology, 1966), p. 145.

[7] Lane, *Early Islamic Pottery*, p. 21.

[8] *Encyclopedia of World Art*, (London: McGraw-Hill, 1963 vol. 8, col. 357.

[9] R. Schnyder, "Tulunidische Lüsterfayence," *Ars Orientalis*, vol. 5 (1963), pp. 49–78.

[10] Whitehouse, "Neutron Activation." H. V. Michel, J. D. Frierman, and F. Asaro, "Chemical Analysis of Ceramic Wares from Fustāt, Egypt," Lawrence Berkeley Laboratory preprint 2387, *Archaeometry*, vol. 18 (1976), p. 85–92.

[11] I. Perlman and F. Asaro, "Pottery Analysis by Neutron Activation," *Archaeometry*, vol. 11 (1969), pp. 21–52.

As the procedure for developing the chemical fingerprint[12] has been previously described, we will only give a brief explanation at this time. Ideally the pottery for the reference group should be excavated material, which is believed to be of local manufacture for stylistic or other reasons, and which, when subjected to neutron activation analysis, is chemically homogeneous. Taking the 18 to 20 selected elements for each sample, the mean value of each elemental abundance for the reference group is determined, and the root-mean-square deviation (σ) from this mean value is calculated for the individual sherds or pots in the reference group. If the average value of the root-mean-square deviation (σ) for approximately 20 elements is 10% or less, the group is considered a good (i.e., sufficiently homogeneous) reference group suitable for classification purposes. When applied to a sample of unknown provenance, agreement with the reference group requires that about 2/3 of the elements should agree within one σ, and very few disagree by more than two σ.

In the course of studies on the provenance of ceramics from Egypt, Iran, and Iraq, 16 lustre ware sherds were analyzed. All of these were archaeologically excavated and this aspect of their history is known. They are stylistically of well-known types that have been discussed in the literature.[13] The 16 sherds consist of eight excavated at Fustat (old Cairo), Egypt; one at Samarra, Iraq; four at Siraf; one at Muveh; and two at Jiruft; these last three sites are in the Fars district of South Iran. As a result of extensive studies of medieval ceramics from Fustat, Siraf, and of the "Samarra" type wares, we have some reference chemical fingerprint groups for provenance determination (Table 2).

LUSTRE GLAZES ON CLAY BODIES

Of our nine samples with clay bodies, four are ninth century polychrome lustres (FUST-8, JIRF-1, 2, and MUVE-1, figs. 1, 2, 3, 4), and five are tenth and eleventh century monochrome lustre wares (FUST-27, 28, 29, 30, and SIRF-7, figs. 5, 6, 7, 8, 9). (See Table 1.)

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[12] F. Widemann, M. Picon, F. Asaro, H. V. Michel, and I. Perlman, "A Lyons Branch of the Pottery-Making Firm of Ateius of Arezzo," *Archaeometry*, vol. 17 (1975), pp. 49–59.

[13] Perlman and Asaro, "Pottery Analysis," p. 35 (see Table 2).

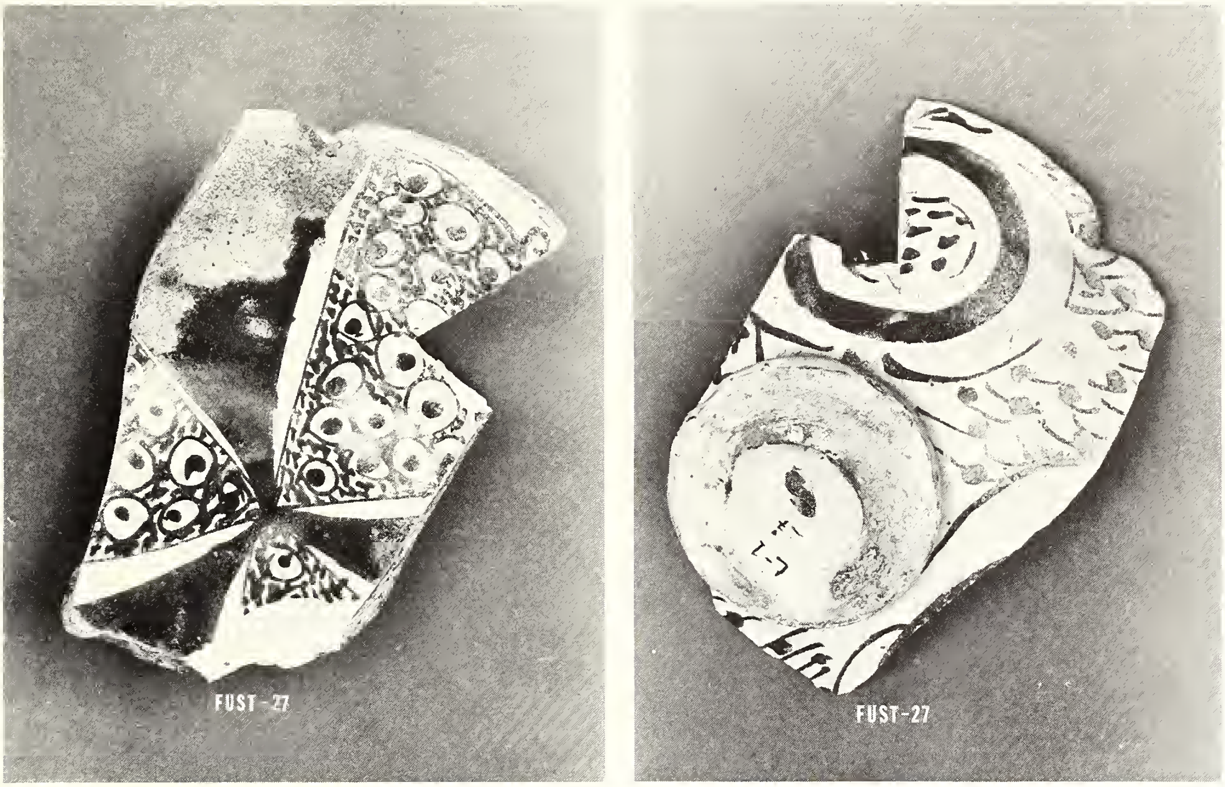

FIG. 5.—FUST-27, 10th century monochrome lustre earthenware, interior, exterior.

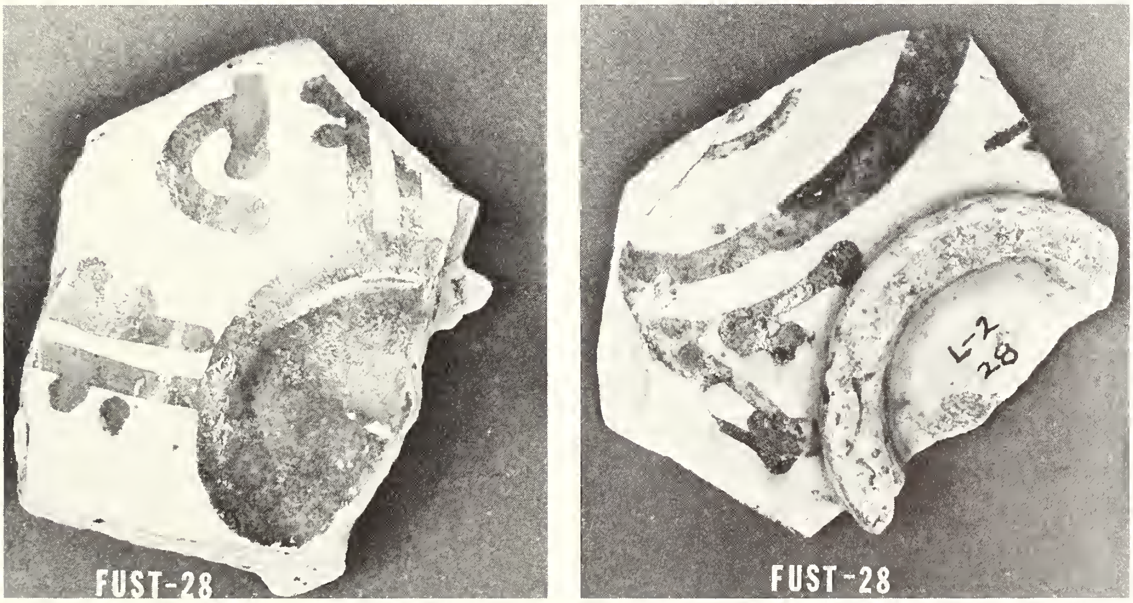

FIG. 6.—FUST-28, 10th century monochrome lustre earthenware, interior, exterior.

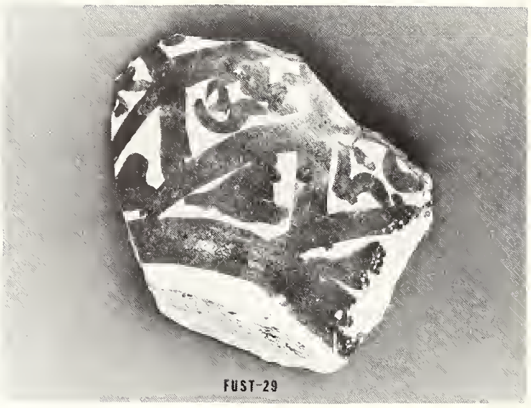

Fig. 7.—FUST-29, 10th century monochrome lustre earthenware.

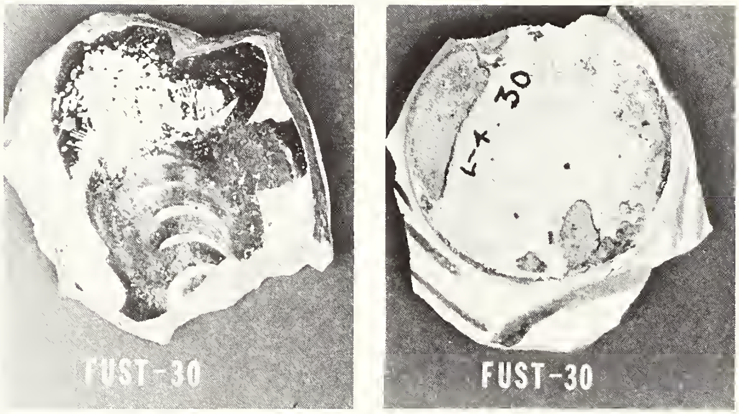

Fig. 8.—FUST-30, 11th century monochrome lustre earthenware, interior, exterior.

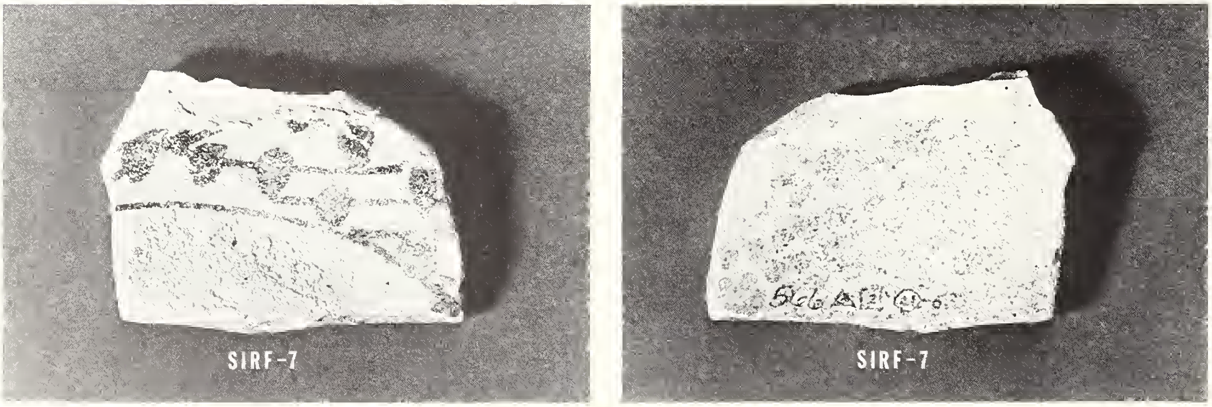

Fig. 9.—SIRF-7, 10th century monochrome lustre earthenware, interior, exterior.

TABLE 1

Observations and Physical Measurements on the Body and Glazes of 16 Early Islamic Lustre Wares

	Century	Body					Glaze					Remarks	Reference to similar pottery
		Hardness (Mohs)	Color (Munsell)	Munsell Name	Texture	Thickness (mm)	Hardness		Thickness (mm)		Type (By XRF[2])		
							Interior	Exterior	Glaze	Slip			
EARTHENWARE *polychrome lustre*													
FUST-8	9th	2.5	5Y8/3	pale yellow	very fine	5.0	6.0	6.0	1.0	0.1	Pb-Sn	Rim sherd	Schnyder, Taf. 1, abb. 2.
JIRF-1	9th	2.5	2.5Y8/4	pale yellow	very fine	5.0	2.5[1]	2.5[1]	0.5	None	Pb-Sn	Rim sherd	V & A, p. 12, fig. 14.
JIRF-2	9th	2.5	2.5Y8/4	pale yellow	very fine	3.0–5.0	2.5[1]	2.5[1]	0.5	0.07	a little Pb-Sn	Base sherd	Schnyder, Taf. 4, abb. 19. V & A, p. 12, fig. 16.
MUVE-1	9th	2.5	2.5Y8/2-4	white/ pale yellow	very fine	4.6–6.5	2.5	Unglazed foot	0.8	0.05	Alk-Sil	Base sherd	V & A, p. 12, fig. 14.
EARTHENWARE *monochrome lustre*													
FUST-27	10th	2.5	5Y8/3	pale yellow	very fine	4.0–5.0	6.75	6.75	Int. 0.7–1.0 Ext. 0.3–0.8	0.02	Pb-Sn	Base, side and rim	Atil, p. 18–19, 20–21. Lane, pl. 13, B.
FUST-28	10th	2.5	2.5Y8/2	white	very fine	4.0–5.0	6.5	5.75	0.3–0.6	0.07	Pb-Sn	Base sherd	Baghat, Pl. VI, 5: Pl. IV, 1 bis.
FUST-29	10th	2.5	5Y8/3	pale yellow	very fine	7.0–15.0	6.5 (3.5)[1]	6.5	0.7	None	Pb-Sn	Base sherd	Baghat, Pl. VI, 3.
SIRF-7	10th	2.5	5Y8/3	pale yellow	very fine	4.0	2.5[1]	2.5[1]	0.3	None	Pb-Sn	Rim sherd	Atil, p. 18–19. Lane, pl. 13, B.
FUST-30	11th	2.5	2.5Y7/2	light gray/light brownish gray	very fine	4.0–5.0	7.0	7.0	0.5–1.0	0.03	Pb-Sn	Base sherd	Lane, pl. 23, B. Baghat, Pl. XV, 3 & 3 bis.
FAIENCE *lustre*													
FUST-9	11th (or later)	3.5	10YR8/2	white	coarse	3.0–4.0	4.5	3.5	0.3–0.6	None	Pb-Sn	Base sherd	Baghat, Pl. XXVI, 1- Pl. XXIX, 2–3.
FUST-31	11th–12th	3.5	10YR7/2	light gray	coarse	4.5	6.75	6.75	0.3	None	Pb-Sn	Rim sherd	Lane, pl. 25, A.
FUST-17	12th–13th	3.5	N10/	white	fine	4.0	6.5	6.5	Int. 0.4 Ext. 0.5	None	Alk-Sil	Body sherd	Atil, p. 140–141.
SAM-120	12th–13th	3.5	N10/	white	fine	4.0	6.5	1.5[1]	0.5	None	Alk-Sil	Rim sherd	ibid
SIRF-121	12th–13th	3.5	10YR8/2	white	very fine	5.0	6.5	6.5	0.5	0.1	Pb-Sn	Body sherd	S.P.A., pl. 631, B. Wilkinson, p. 65, 13C.
SIRF-122	12th–13th	3.5	10YR8/2	white	very fine	6.5–8.0	6.5	6.5	Int. 1.0 Ext. 0.7–0.8	0.1	Pb-Sn	Rim sherd	Ibid
SIRF-130	12th–13th	3.5	N10/	white	very fine	3.0	7.0	6.75	0.2	None	Pb-Sn	Body sherd	Ibid

[1] Devitrified glaze deterioration

[2] XRF x-ray fluorescence spectroscopy

References:

Atil E. Atil *Ceramics From the World of Islam* (Washington, D.C.: Freer Gallery of Art, 1973

Baghat A. Bey Baghat and F. Massoul, *La Céramique Musulmane de L'Egypte* (Cairo: L'Institut français d'archeologie oriental 1930)

S.P.A. A.U. Pope and P. Ackerman, *A Survey of Persian Art*, Vol. 5 (London, Oxford 1938)

Schnyder R. Schnyder, "Tulunidische Lusterfayence," *Ars Orientalis*, Vol. 5 (1963), pp. 49–78

V & A Victoria and Albert Museum, *Islamic Pottery 800–1400 A.D.* (London: An exhibition arranged by the Islamic Art Circle, 1969)

Wilkinson C.K. Wilkinson *Iranian Ceramics* (New York: Metropolitan Museum of Art, 1963).

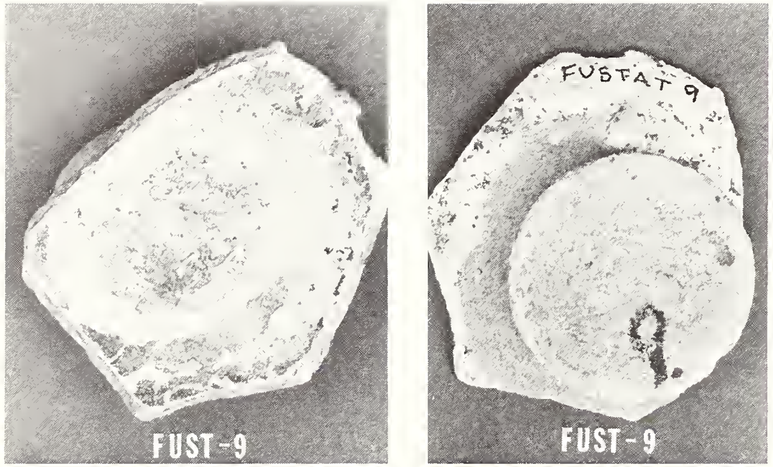

Fig. 10.—FUST-9, 11th century or later lustre faience, interior, exterior.

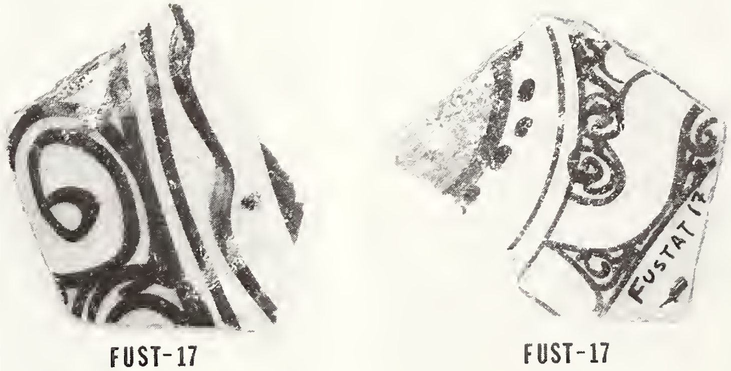

Fig 11.—FUST-17, 12th–13th century lustre faience, interior, exterior.

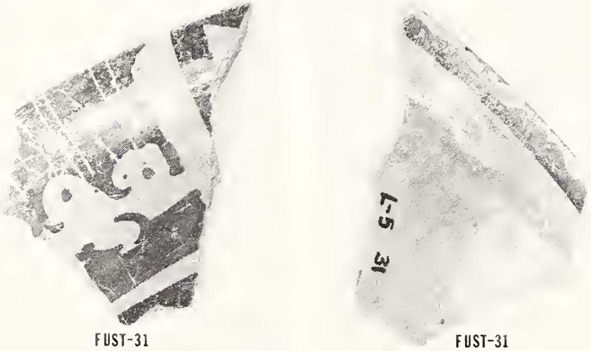

Fig. 12.—FUST-31, 11th–12th century lustre faience, interior, exterior.

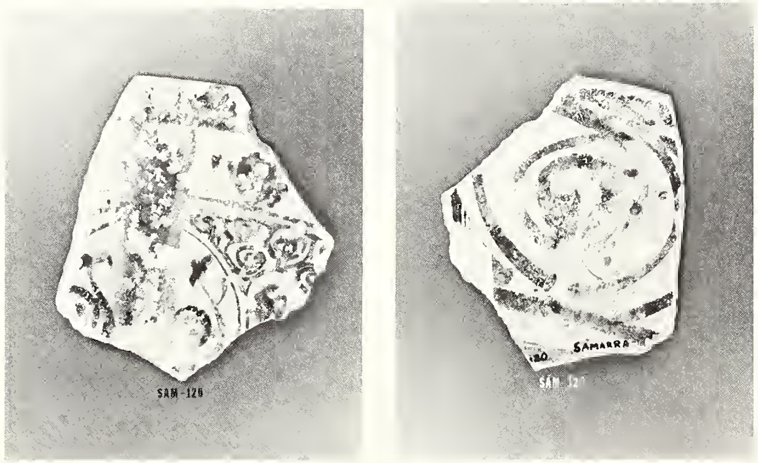

Fig. 13.—SAM-120, 12th–13th century lustre faience, interior, exterior.

Fabrics

Eight of the sherds have the typical pale yellow to white "Samarra" clay body. FUST-30 has a light brownish gray color and is chemically unlike the other eight. The hardness for all sherds is 2.5 (Mohs scale, scratch test) taken from a freshly broken surface. This is midway between gypsum (2) and calcite (3). The texture is uniformly very fine, the only inclusions noted are occasional grains of translucent clastic quartz up to 0.5 mm in diameter (FUST-29, SIRF-7); these clays appear to be carefully levigated. The vessels were all made on the fast potter's wheel and are evenly and thoroughly kiln fired. The body thicknesses average 4.0–5.0 mm with the exception of FUST-29 which is a rather heavy base sherd, 7.0–15.0 mm thick.

Glazes

The glazes are in excellent condition except for the Iranian samples which are much devitrified presumably by the heat, salinity, and humidity of the Persian Gulf environment, but even these still show excellent adhesion between lustre, glaze, and body, and retain much of their structure. The glazes tend to be thick, 0.3–1.0 mm, tin-opacified lead glazes except for MUVE-1 which is an alkali-silicate glaze. The opacity is variable; FUST-30 is completely opaque while others, when examined under a binocular microscope at ×30, reveal that the apparent opacity is due to small irregular opaque white masses and thin veils in a transparent glaze. With the microscope it is generally possible to see between these opaque masses to the interface between the body and the glaze. However, to the naked eye they seem completely opaque.

FUST-27, 28, 29, and 30 are in excellent preservation and the color of the metallic lustre is a yellow gold by reflected light; at 30 power magnification they have a distinctly olive green undertone. FUST-8 is a polychrome lustre of transparent garnet, brownish red and yellow gold. SIRF-7 and FUST-27 are both monochrome lustre ware and stylistically close, but the Siraf glaze is almost completely devitrified. The Muveh and Jiruft polychrome lustre wares show moderate deterioration but still preserve some glaze especially in the lustred areas. JIRF-1,2 and MUVE-1 are all green-and-brown-metallic polychrome lustres.

LUSTRE GLAZES ON FAIENCE BODIES

The seven faience sherds are an extremely diverse group. Three were excavated at Fustat (FUST-9, 17, 31, figs. 10, 11, 12) one at Samarra (SAM-120, fig. 13) and three at Siraf (SIRF-121, 122, 130, figs. 14, 15, 16). FUST-9 and 31 are probably Egyptian[14] of the eleventh and twelfth centuries. FUST-17 and SAM-120 have designs that are close to North Syrian faience of the Rakka-Rusafa type and may be from the late 12th to the first half of the 13th century. The Siraf faience lustres are similar to Iranian or Iraqi Seljuk wares which date from the latter part of the twelfth to the first third of the thirteenth century (Table 1).

Fabrics

The two Egyptian sherds (FUST-9 and 31) have coarse bodies; 9 is creamy white and 31 is light gray. FUST-17 and SAM-120 have

[14] See note 10.

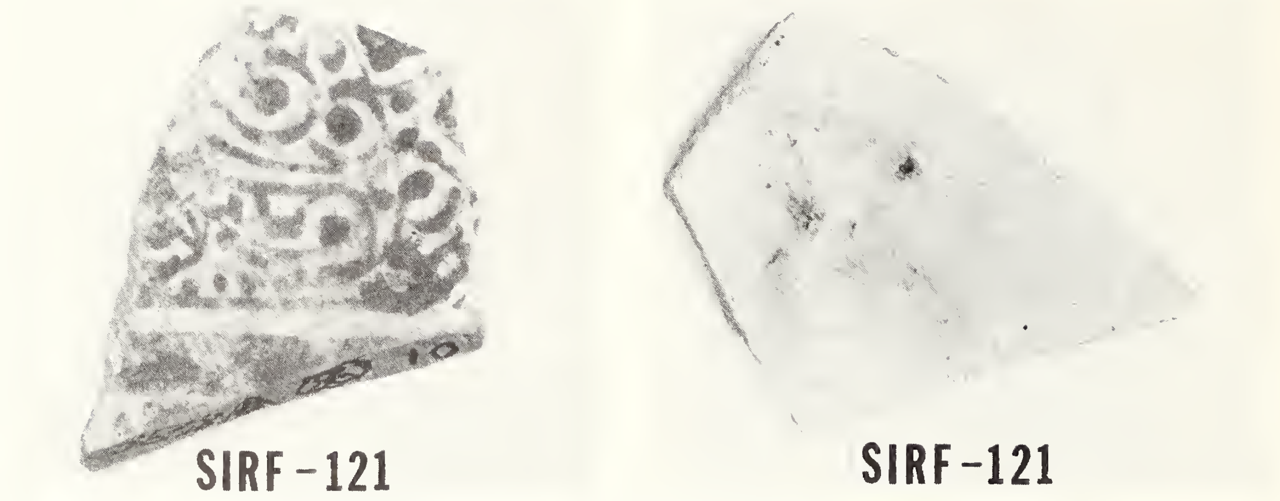

Fig. 14.—SIRF-121, 12th–13th century lustre faience, interior, exterior.

pure white, coarse sugary textured bodies. SIRF-121, 122, 130 have pure white, fine sugary textured bodies which are minutely porous; they are of the same provenance as some monochrome glazed faiences excavated at Siraf (SIRF-131, 132, 134, 135). The hardness taken from a freshly broken surface is 3.5 (Mohs scale) which is between calcite (3) and fluorite (4) and is low for such fine thin ware. At 30 power magnification little

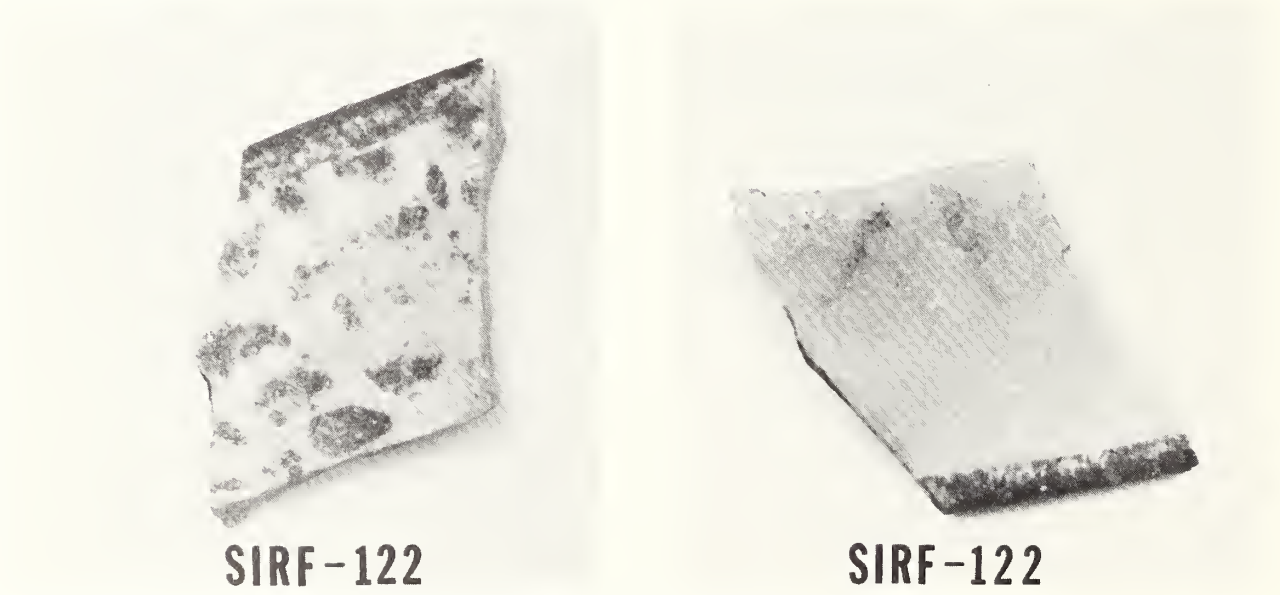

Fig. 15.—SIFR-122, 12th–13th century lustre faience, interior, exterior.

vitrification is visible which probably explains the rather low hardness. It is possible that the low hardness may point to a somewhat earlier date for it seems that the faiences of the earlier part of the twelfth century tend to be less highly vitrified than the later works.[15]

Glazes

The glazes are in good to excellent condition on all sherds, with excellent adhesion between glaze and body. FUST-9 has a glaze that is somewhat runny and has gathered in thick drops near the base. Since this faience bowl has a tin-opacified lead glaze which is hardly necessary on the pure white faience, it may be a transitional form between clay body lustre and faience body. The potter's lack of experience manifests itself in this too fluid glaze. The glaze on FUST-9 is softer than the others which have an average hardness of 6.5 (Mohs scale), between feldspar (6) and quartz (7); the interior is 4.5 and the exterior 3.5. There is some slight surface deterioration visible under the microscope.

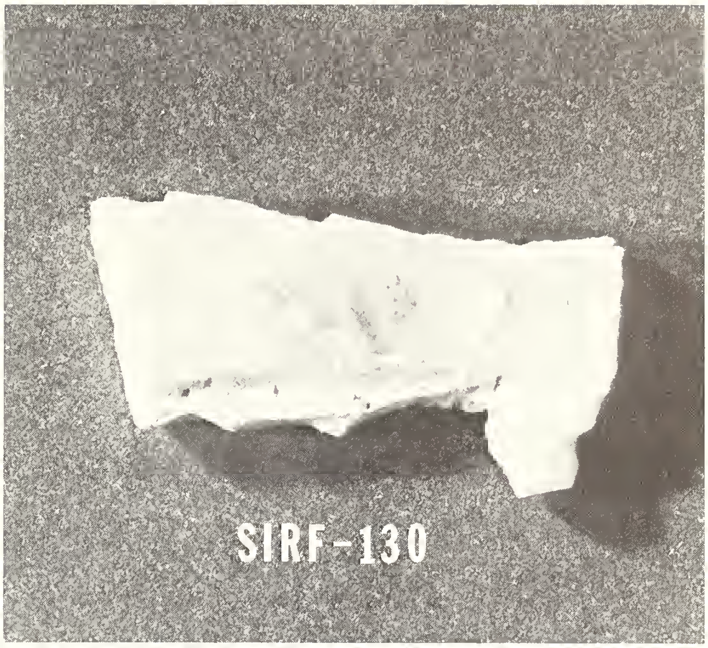

Fig. 16.—SIRF-130, 12th–13th century lustre faience.

FUST-31 has an attractive turquoise glaze which contains little lead and is slightly opacified with time. It contains many bubbles and undigested transparent quartz or glass frit particles up to 0.5 mm in diameter. The umber brown lustre with slight metallic quality is in the form of a kufic inscription. The glaze penetrates the very coarse body and is 0.3 mm thick.

The two sherds of probable Syrian origin, FUST-17 and SAM-120, have transparent clear alkali-silicate glazes. FUST-17 has an ultramarine-blue colored cobalt under-glaze and SAM-120 has a turquoise-blue copper under-glaze. The lustre paintings are purple brown with some metallic reflections. The glazes are 0.4 to 0.5 mm thick. Their hardness is 6.5 (Mohs) however, the Samarra

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[15] J. W. Allan, L. R. Llewellyn, and F. Schweizer, "The History of so-called Egyptian faience in Islamic Persia: Investigations into Abū'l-Qāsim's treatise," *Archaeometry*, vol. 15 (1973), pp. 165–173, and "Some observations on the origins of the medieval Persian faience body," in W. Watson, ed., *Art of Iran and Anatolia from the 11th to the 13th century A.D.* (Colloquies on Art and Archaeology in Asia, No. 4), (London: Sir Percival David Foundation, 1973), pp. 60–67. These articles hypothesize the possibility of separating the eleventh and earlier twelfth century faience from the well known products of the late twelfth and early thirteenth century. In the light of the inconclusive results of the chemical analysis, we would suggest that there is some evidence to indicate that the change may be in the degree of vitrification, which can be easily determined by a simple hardness test, and verified by scanning electron microscopy. A survey of this sort may indeed yield useful information.

TABLE 2

Chemical Composition of Clay-Bodied Lustre Ware and Reference Groups

	Lustre Ware and Polychrome Lustre	Iran Lustre Ware		Siraf "Samarra" Ware	Egyptian "Nile Mud" Ware
No. of pieces in group	4: (FUST-8,27,28,29)	4: (JIRF-1,2,MUVE-1, SIRF-7)	1: (FUST-30)	12	32
σ[4]	7%	11%		8.4%	8%
Element					
Al%	6.07 ± .12[2]	6.34 ± .55[2]	7.36 ± .12[3]	6.36 ± .30[2]	—
Ca%	13.9 ± .3	—	10.2 ± .6	13.2 ± 1.0	2.58 ± .84[2]
Mn	950 ± .50	951 ± 72	724 ± 8	899 ± 40	1204 ± 68
Na%	1.41 ± .16	1.28 ± .35	1.44 ± .02	1.65 ± .11	1.355 ± .215
K%	.92 ± .33	.99 ± .31	.93 ± .23	.87 ± .48	—
U	1.96 ± .05	2.18 ± .13	2.41 ± .03	2.11 ± .15	2.26 ± .41
Ba	172 ± 14	245 ± 52	343 ± 15	182 ± 47	493 ± 74
Sm	4.04 ± .11	4.10 ± .27	6.86 ± .01	4.05 ± .12	—
La	21.7 ± 1.0	23.1 ± 1.2	35.4 ± .7	22.6 ± .7	32.8 ± 1.2
Ti%	.40 ± .03	.50 ± .15	.76 ± .02	.43 ± .04	.996 ± .049
Lu	.316 ± .017	.308 ± .026	.429 ± .019	.313 ± .02	.512 ± .027
Co	26.9 ± 1.9	28.1 ± 2.1	25.5 ± .4	26.9 ± 1.5	34.96 ± 1.60
Sc	19.16 ± .56	19.00 ± 1.61	18.57 ± .06	18.72 ± .52	23.11 ± .96
Fe%	5.01 ± .12	5.04 ± .39	5.91 ± .08	4.91 ± .19	6.82 ± .24
Cs	3.2 ± 1.1	2.9 ± .6	1.4 ± .2	3.5 ± 1.2	1.39 ± .21
Cr	260 ± 13	268 ± 23	136 ± 3	257 ± 22	181 ± 16
Th	7.125 ± .031	7.33 ± .58	8.12 ± .12	7.15 ± .11	6.94 ± .49
Eu	1.019 ± .025	1.041 ± .070	1.782 ± .015	1.007 ± .030	—
Ce	46.4 ± 1.1	48.2 ± 3.1	76.3 ± .9	46.2 ± 1.2	—
Hf	3.34 ± .06	3.26 ± .25	6.59 ± .11	3.26 ± .16	8.67 ± .75
Ta	.814 ± .018	.825 ± .051	1.388 ± .007	.799 ± .035	1.445 ± .106

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[1] Data taken from I. Perlman and F. Asaro, *Archaeometry*, vol. 11, no. 21 (1969), p. 35.

[2] The values in this column are the average abundances in parts-per-million (or % if so indicated) and the standard deviation

[3] The values in this column are the abundance in parts-per-million (or % if so indicated) and the counting error.

[4] σ is the average value of the root-mean-square deviation, in percent, of 20 elements in the group.

sherd had areas that are moderately devitrified and quite soft.

SIRF-121, 122, and 130 are Seljuk faiences, probably of the twelfth century. The glazes are slightly tin-opacified giving them a milky translucence. The lustre is of rather poor quality, light green to light olive with pale brown markings in the center of the broad lines and a very thin faint red areole at the edges. The glazes are 0.5 to 1.0 mm thick with the exception of the very thin SIRF-130 whose total thickness is 3.0 mm for interior and exterior glazes and body. In this case the glaze is 0.2 mm thick. The glaze hardness is 6.5 for SIRF-121, 122 and 7.0 for SIRF-130.

RESULTS

The four Fustat earthenware sherds, FUST-8, 27, 28, 29, have chemical composition patterns which are in excellent agreement with Samarra ware sherds excavated at Siraf, which have been demonstrated[16] by neutron activation analysis to be of Mesopotamian origin. The four Iranian herds (JIRF-1,2, MUVE-1, SIRF-7) also have the same chemical composition as the Fustat pottery and Samarra ware and thus the same provenance. Twenty-one elements were used in the comparison (Table 2). Besides the Fustat lustre wares, data is shown for the reference group of Samarra ware sherds from Siraf and the lustre wares from Siraf, Muveh, and Jiruft. For comparison FUST-30, an eleventh century lustre, is also shown. This has a calcareous clay body unlike the other groups but similar to several Egyptian sherds. Figure 17 shows the abundance of aluminum, samarium, tantalum, and chromium for the various groups of sherds. The first bar indicates the average content for the twelve pieces of Samarra ware, i.e., 6.4% Al. The hatched area shows the root-mean-square deviation (σ) for the twelve. Generally the spread is substantially larger than the experimental error and represents the variation in the pottery. For each element, the second bar shows the same information for a group of four lustre sherds excavated in Iran, JIRF-1, 2, MUVE-1 and SIRF-7. The third bar shows values for the four Fustat earthenware lustres FUST-8, 27, 28, 29. The last bar shows the value for a single eleventh century earthenware sherd FUST-30. The blacked-in area (Sm, Ta, Cr, for FUST-30) shows the experimental uncertainty and is typical of the measurements. The elemental abundances are in parts per million, those in percent are so indicated after the element name.

As seen in Table 2, our Fustat and Iranian ninth–tenth century earthenware lustres agree very well with the Samarra ware from Siraf of Iraqi origin. They also agree with the Sassanian glazed ware and Early Turquoise ware found at Siraf which were also imported from Iraq.[17] They are distinctly different from FUST-30 an eleventh century earthenware lustre sherd (see chromium, samarium, and tantalum, fig. 17). They are also different from Egyptian pottery made from Nile silt. Thus, it would appear that the Fustat and Iranian ninth and tenth century earthenware lustre sherds are very likely to share an Iraqi origin. The chemically different FUST-30, eleventh century earthenware lustre, is

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[16] See note 10.

[17] F. Asaro, H. V. Michel, and J. D. Frierman, "Provenance of Glazed Near Eastern Pottery from Sīrāf." Lawrence Berkeley Laboratory preprint 2955, to be published. Paper presented at the Annual meeting of American Oriental Society, March 1974, Santa Barbara, California.

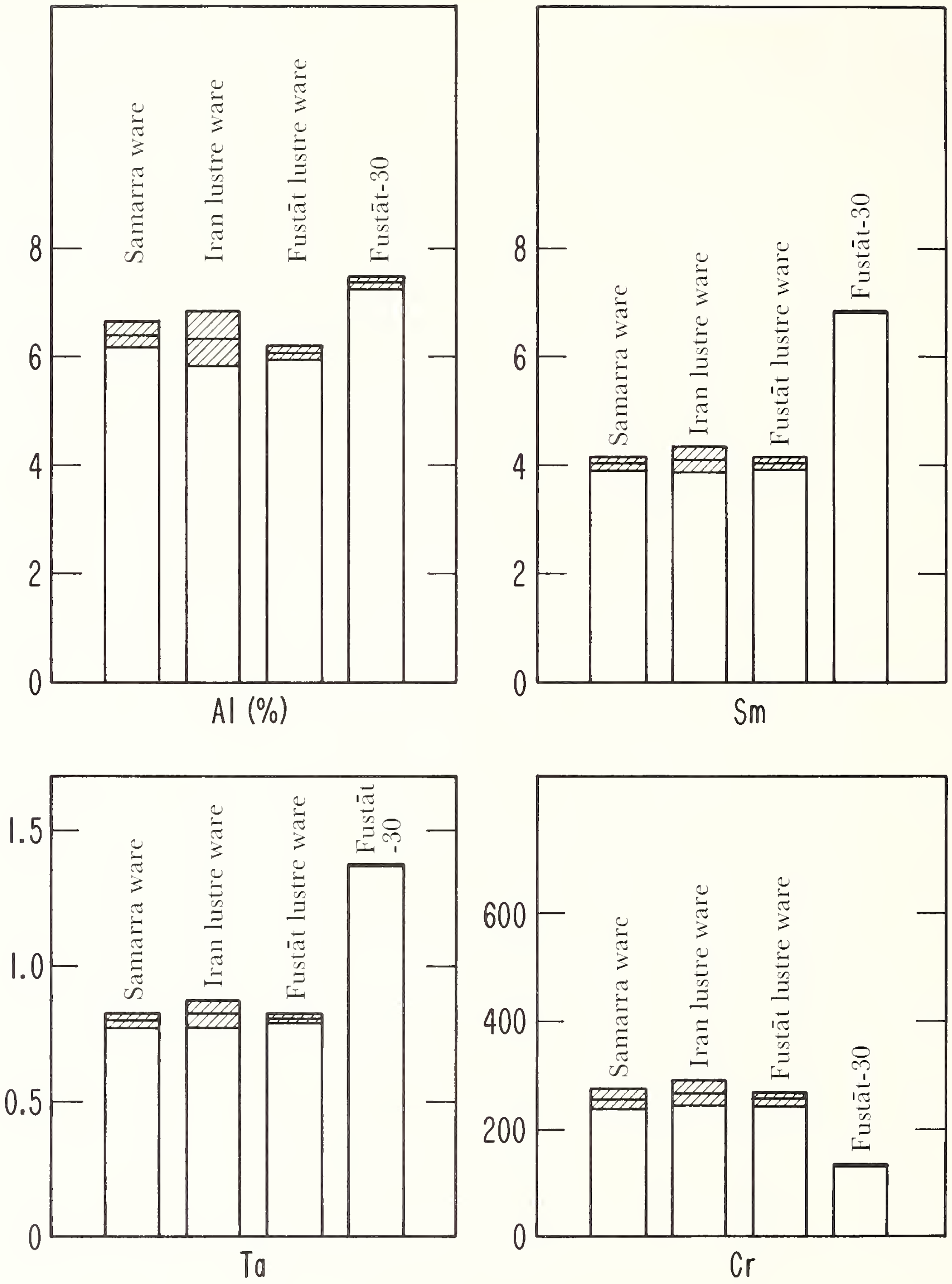

Fig. 17.—Abundances of aluminum, samarium, tantalum, and chromium for two groups of lustre ware, reference Samarra ware, and FUST-30, in ppm or % if indicated.

TABLE 3

Chemical Composition of Faience-Bodied Ware Excavated in Fustat, Egypt, and Reference Groups

	Fustat Waster and Lustre Ware	Underglaze Painted faience			
No. of pieces in group	6: (FUST-3,4,9,10,15,31)	5: (FUST-12,13,14,19,20)	1: (FUST-17)	1: (SAM-120)	3: (SIRF-121,122,130)
σ[4]	20% (20 elements)	25% (20 elements)			
SiO_2%	[87][1]	[89][1]			
Al%	2.40 ± .36[2]	.81 ± .18[2]	1.34 ± .05[3]	1.59 ± .13[3]	4.34 ± .26[2]
Mg%	<2.	<1.8	<2.	<2.	<2.
Ca%	2.6 ± .9	4.8 ± 1.6	3.1 ± .5	2.47 ± .4	1.89 ± .6
Mn	148 ± 62	420 ± 180	179 ± 3	181 ± 3	89 ± 6
Na%	2.05 ± .25	1.08 ± .26	1.67 ± .02	1.70 ± .02	2.71 ± .46
K%	.78 ± .15	.51 ± .10	.69 ± .17	.61 ± .18	1.35 ± .19
U	1.06 ± .21	1.15 ± .17	.55 ± .02	.54 ± .02	2.07 ± .14
Ba	99 ± 41	116 ± 20	60 ± 9	52 ± 8	154 ± 40
Sm	1.97 ± .23	1.06 ± .18	.748 ± .005	.727 ± .005	4.98 ± .97
La	12.3 ± 1.1	7.0 ± 1.6	3.6 ± .4	4.1 ± .4	26.7 ± .5
Ti%	.189 ± .044	.049 ± .020	.063 ± .015	.057 ± .012	.657 ± .047
Lu	.125 ± .015	.079 ± .014	.077 ± .010	.066 ± .010	.488 ± .026
Co	4.4 ± 1.9	6.5 ± 3.0	6.5 ± .1	6.1 ± .1	2.06 ± .09
Sc	4.69 ± .57	1.91 ± .56	3.57 ± .02	3.45 ± .02	15.1 ± 4.0
Fe%	.99 ± .19	.39 ± .10	.99 ± .02	.93 ± .02	.43 ± .03
Cs	.57 ± .15	.34 ± .13	.80 ± .10	.80 ± .10	1.66 ± .15
Cr	33.0 ± 2.5	138 ± 91	80 ± 2	116 ± 2	19.2 ± .3
Th	2.92 ± .38	1.44 ± .29	1.28 ± .05	1.30 ± .05	10.66 ± .21
Eu	.458 ± .043	.239 ± .037	.197 ± .004	.199 ± .004	1.182 ± .018
Ce	24.1 ± 2.7	12.1 ± 2.3	8.4 ± .3	7.9 ± .3	56.1 ± 2.7
Hf	2.24 ± .56	2.57 ± .53	.55 ± .04	.59 ± .04	8.71 ± .01
Ta	.48 ± .07	.16 ± .02	.134 ± .002	.128 ± .002	.92 ± .04

[1] The SiO_2 content was determined by difference to 100%.

[2] The values in this column are the average abundances in parts-per-million (or % if so indicated) and the standard deviation of the abundances.

[3] The entries in this column are the composition and the counting error.

[4] σ is the average value of the root-mean-square deviation, in percent, of 20 elements in the group.

roughly similar to a few pieces from Nag-ed-Deir and may be of Egyptian origin although we cannot make a definite assignment.

The comparisons are not as definite for faience as for pottery because the synthetic faience bodies form groups whose compositions are not as homogeneous as pottery, i.e., they show 20–25% standard deviation for twenty elements. In addition many fewer sherds have been subjected to neutron activation analysis.

In Table 3 are shown data for a group of four waster sherds of Egyptian faience excavated at Fustat (Fustat Fatimid sgraffiato and monochrome celadon ware) and two lustre ware sherds FUST-9 and 31; and the Underglaze Painted Faience excavated at Fustat but stylistically different and probably of Iranian origin.[18] The Egyptian faience is easily distinguishable chemically from the Underglaze Painted Faience. FUST-9 and 31 are probably of Egyptian origin, because they are chemically similar to the four Fustat waster sherds.

FUST-17 and SAM-120 are stylistically and chemically similar. As seen in Table 3, they are distinctly different in chemical composition from Egyptian faience or the probable Iranian Underglaze Painted Faience. They are typical of the North Syrian Rakka–Rusafa type wares of the late twelfth and early thirteenth centuries in both technique and design.

The Seljuk faience sherds from Siraf, SIRF-121, 122, 130 are members of a larger chemical group of clear and turquoise glazed faiences excavated there. There is no evidence of their manufacture at Siraf and they do not match the Egyptian and Underglaze Painted Faience. It is interesting to note that the same manufacturers produced both the monochrome glazed and the lustre decorated vessels excavated at Siraf. The analyses are roughly like the main group of faiences although they do not conform as closely as the earthenware group members do. Such variations have been observed in the Egyptian faience, the probably Iranian Underglaze Painted Faience and the North Syrian Rakka–Rusafa faience. This is the result of the nature of the faience bodies being synthetically made by mixing ingredients—quartz or quartzite, frit and clay from various sources.

This work on a limited number of early Islamic earthenware lustre sherds suggests that 9th and 10th century lustres found in diverse locations were produced in Iraq and that by the end of the 12th century lustre painting was being done in Egypt, Syria, Iraq and Iran. Although this is not a large sampling it does offer some objective answers to the vexatious problem of the origin of early Islamic lustre wares.

ACKNOWLEDGEMENTS

The sherds discussed in this article were most generously supplied by the excavators of the sites: Fustat, George Scanlon; Siraf, David Whitehouse; Samarra, the Iraq Museum, Baghdad; Jiruft and Muveh, the late Andrew Williamson. We wish to acknowledge their kind assistance. We are grateful to the staff of the Berkeley Triga Reactor for the neutron irradiations used in this work and the L.B.L. Safety Services Department for rapid delivery of the irradiated samples. We thank Duane Mosier, James E. Arnold, David Gok and Julie Rodriquez Jones for their continual assistance. We also wish to thank Barbara Branstetter and photographer Susan Einstein for their help.

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[18] See note 10.

DECOR REPLICATION IN TWO LATE CHOU BRONZE *CHIEN*

By BARBARA W. KEYSER*

INTRODUCTION

Many scholars have studied the technical problems of Shang bronzes, but only recently have they considered those of late Chou bronzes, which differ considerably from earlier examples in technique as well as style.[1]

One of the most important stylistic sequences of the late Chou period developed in the sixth and fifth centuries B.C. and is characterized by vessels decorated with interlaced zoomorphic forms in horizontal bands extending around their circumferences. Unlike Shang bronzes, these works often bear identical repeated elements, either on a single vessel or in a series of vessels. The ways in which late Chou founders extended aspects of Shang technical tradition and introduced new techniques for rendering this style of bronze decor have only begun to be explored.

This paper presents a detailed analysis of the techniques of decor replication in two specific late Chou vessels belonging to the interlaced zoomorphic stylistic sequence. The bronzes chosen for study are a pair of *chien*: one is in the Freer Gallery of Art[2] (fig. 1); the other in the Minneapolis Institute of Arts[3] (fig. 2). According to Freer Gallery of Art acquisition records, both *chien* were said to have been excavated in 1938 at Hui-hsien in Honan province (see fig. 3). Both then appeared in the collection of C. T. Loo in New York and were bought by the Freer Gallery of Art and Alfred F. Pillsbury, who donated his collection to the Minneapolis Institute of Arts.

These *chien* are ideal subjects for study in several respects. First, they are of great importance historically since, unlike most late Chou bronzes, they can be dated from their inscriptions and play a vital role in establishing a late Chou stylistic chronology. From the technical point of view, these vessels provide an unusually clear opportunity to study the techniques by which late Chou founders used identical decor modules to construct the patterns and/or molds for casting a series of vessels. The pair allow us to compare replication techniques on different parts of one vessel, and on two different vessels. Further, these findings underscore the distinctions between Shang and Chou foundry practice.

Both *chien* bear decor in three registers separated by panels of braid; a similar plait appears on the foot. The top and bottom

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* Conservator, Fine Arts, National Gallery of Canada, Ottawa.

[1] Barbara W. Keyser, "A Technical Study of Two Late Chou Bronze *Chien*," *Bulletin of the American Institute for Conservation of Historic and Artistic Works*, vol. 13, no. 2 (1973), pp. 50–64. Noel Barnard, "Notes on Selected Bronze Artifacts," *Proceedings of a Symposium on Scientific Methods of Research in the Study of Ancient Chinese Bronzes and Southeast Asian Metal and Other Archaeological Artifacts* (Melbourne: National Gallery of Victoria, 1975) pp. 47–82. Wan Chia-pao, "A Comparative Study of the Casting of Bronze *Ting*-cauldrons from An-yang and Hui-hsien," *Proceedings of a Symposium on Scientific Methods of Research* (Melbourne: National Gallery of Victoria, 1975) pp. 17–46.

[2] John A. Pope, Rutherford J. Gettens, James Cahill, and Noel Barnard, *The Freer Chinese Bronzes*, vol. 1 (Washington, D.C.: Smithsonian Institution, 1967), p. 478.

[3] Bernhard Karlgren, *A Catalogue of the Chinese Bronzes in the Alfred F. Pillsbury Collection*, (Minneapolis: University of Minnesota Press, 1952), p. 138.

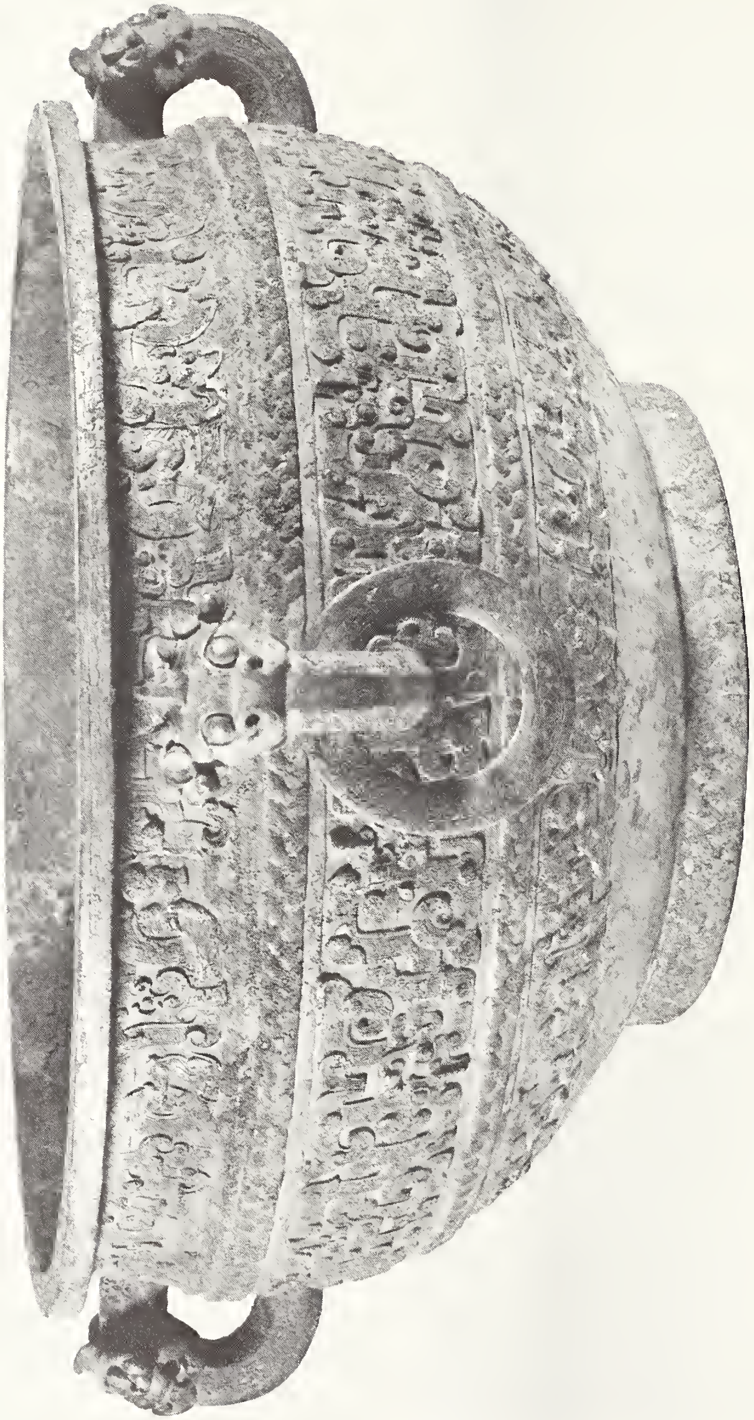

FIG. 1.—*Chien*, Freer Gallery of Art, Washington, D.C. (Accession No. 39.5).

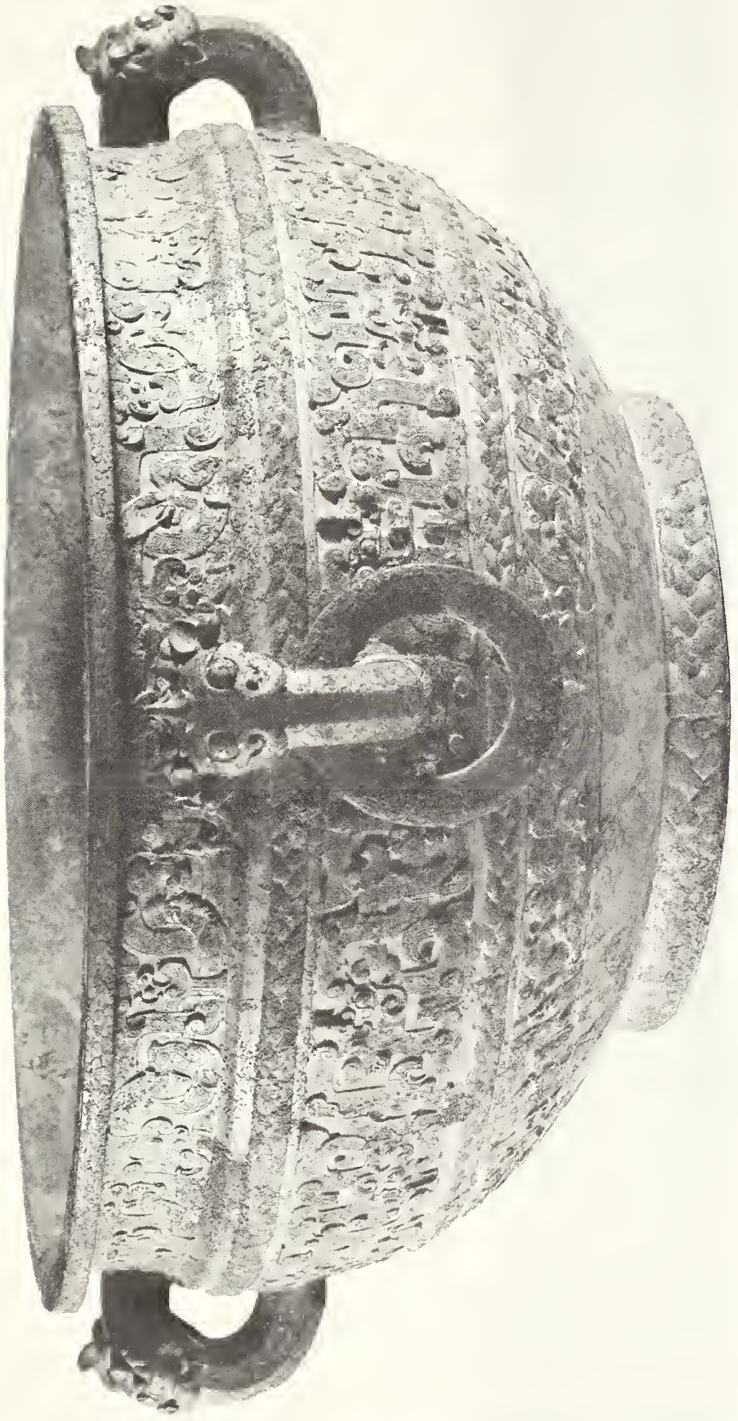

Fig. 2.—*Chien,* The Minneapolis Institute of Arts, Minneapolis (Accession No. 50.46.103).

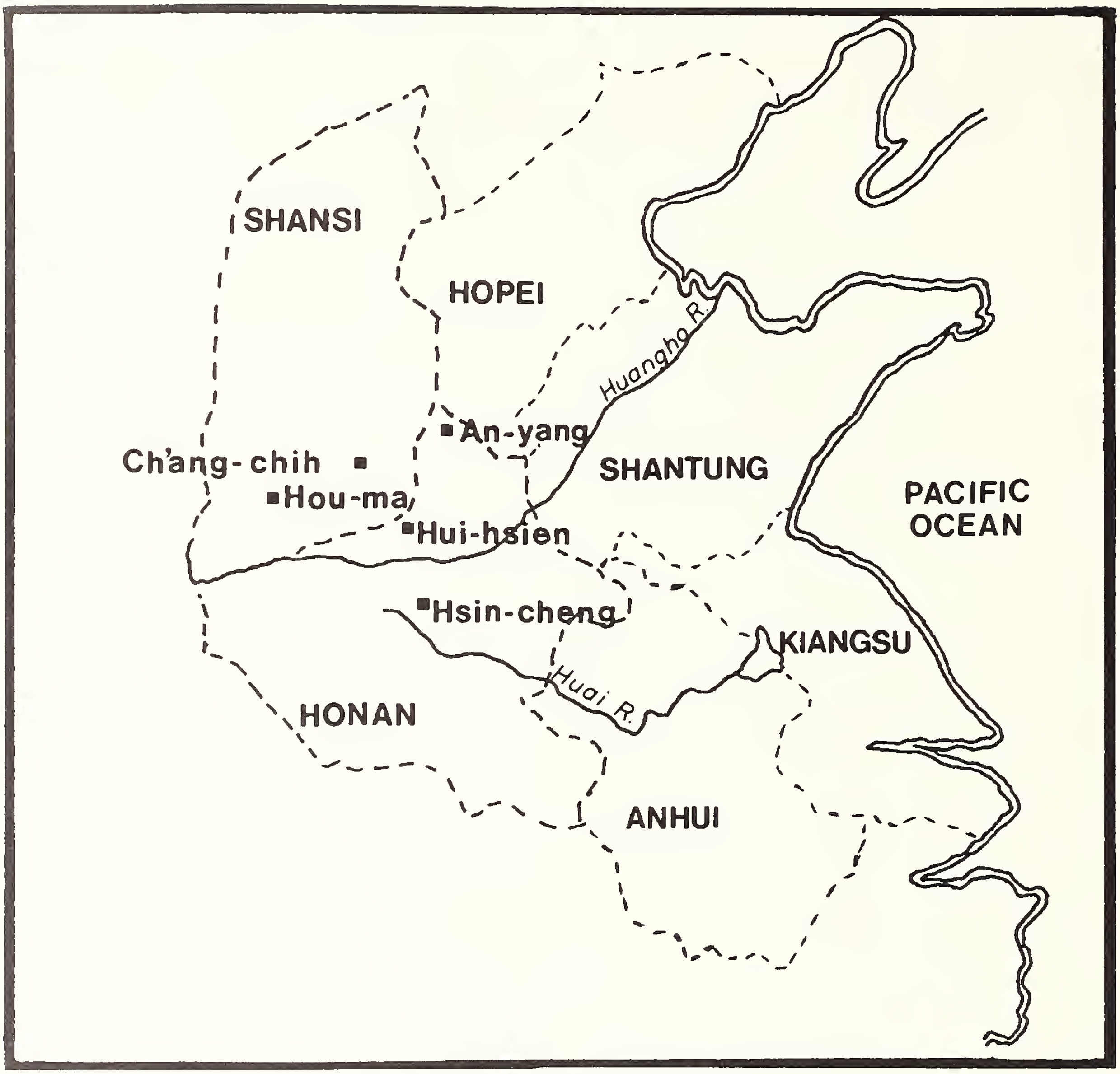

FIG. 3.—Map of Northeast China showing sites mentioned in the text.

belts of decor consist of interlaced bird-dragons[4] with each second creature having its head closer to the lower margin of the band and the intervening creatures having their heads closer to the upper. The central band consists of monster masks, each with two serpentine bodies interlaced to produce a symmetric design about each mask. Every second mask is seen upright as the vessel stands; the others are inverted. A narrow band of cowries appears on the side of the vessel's lip. On the upper surface of the lip is

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[4] Decor terminology here follows George Weber, *The Ornaments of Late Chou Bronzes: A Method of Analysis* (New Brunswick, New Jersey: Rutgers University Press, 1973), pp. 83–90.

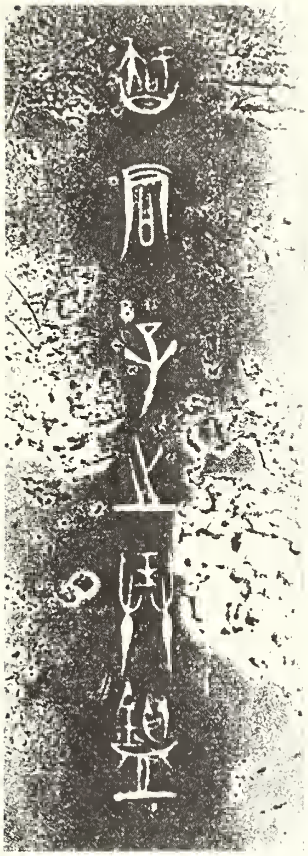

Fig. 4.—Rubbing of inscription of the Freer *chien*.

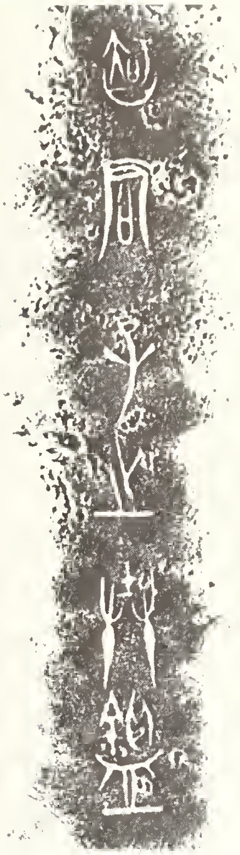

Fig. 5.—Rubbing of inscription of the Minneapolis *chien*. (Courtesy The Minneapolis Institute of Arts).

a second type of interlaced dragon; the same motif decorates the rings which depend from two of the four handles on each *chien*. The handles are octagonal in section with a geometric design of "V" and "M" forms on three alternating surfaces. Each handle issues from the mouth of a three-dimensionally modelled monster head.

Both vessels bear the same six-character inscription (figs. 4 and 5). It is translated "The esteemed *chien* of the son of the ruler of Chih"[5] or "*Kien*-vessel [to be] handled [i.e. used] by the nobleman Chi"[6]. Most scholars agree that the inscription refers to the powerful Chih family of the state of Chin, and, since this family was extinguished in 453 B.C., that the vessels were made in the second quarter of the fifth century B.C. Thermoluminescence data from samples of the ceramic core material in the handles and foot of the Freer *chien* are consistent with such a date.[7]

ANCIENT CHINESE FOUNDRY PRACTICE

At the outset it is important to discuss the facts about ancient Chinese foundry practice

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[5] Pope *et al.*, *The Freer Chinese Bronzes*, vol. 1, p. 483.

[6] Karlgren, *Catalogue*, p. 138.

[7] Thermoluminescence dating by Stuart Fleming, Research Laboratory for Archaeology and the History of Art, Oxford, England. "Using standard methods and techniques it is estimated that the material of the sample was first fired between 1090 and 2640 years ago". Private communication, 1972.

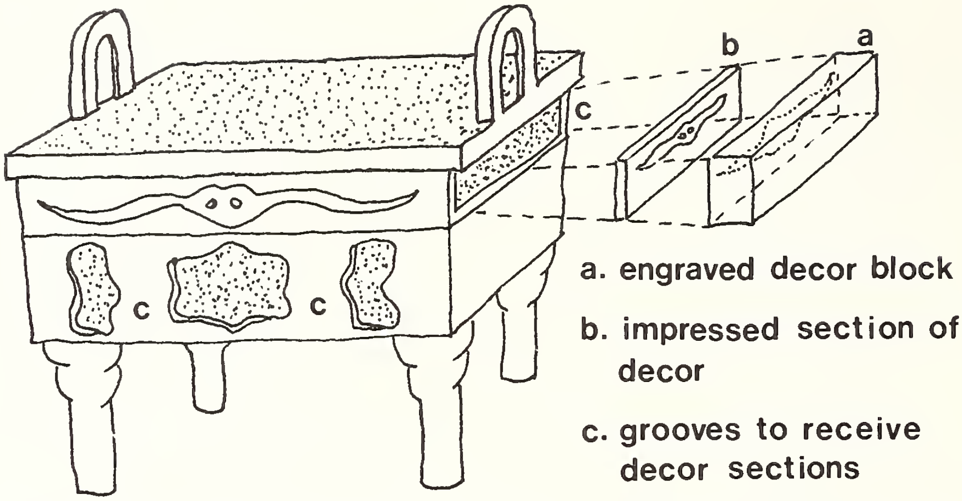
a
b
c
c
c
a. engraved decor block
b. impressed section of decor
c. grooves to receive decor sections

FIG. 6.—Sectional pattern construction according to Barnard (after *Bronze Casting and Bronze Alloys in Ancient China*, Figure 24).

already established by scholars, as well as some of the speculative theories proposed by them. Important issues include: materials and designs of molds and patterns (often called models);[8] methods of casting and joining appendages; whether patterns and/or molds are constructed in a modular way; whether decor motifs were replicated from master pattern blocks, and if so, at what period did this practice begin; and to what extent decor was applied to the pattern or directly in the mold surface. Of equal importance is the fact that scholars are beginning to delineate the evolution of casting techniques which accompanied stylistic change in the Shang and Chou periods.

A pioneer in these studies was Orvar Karlbeck, whose study in 1935 of mold fragments from the Shang foundry site at An-yang led him to conclude that ceramic piece molds rather than the *cire-perdue* technique were used to cast early Chinese bronzes. Karlbeck believed that a ceramic pattern was sculpted and clay piece molds for casting were impressed from it.[9]

In the 1960's other writers extended Karlbeck's basic concepts. Wilma Fairbank stressed the interrelationship between the ceramic and metallurgical phases of the Chinese bronze casting process. She believes that the well-developed ceramic technology of prehistoric China accounts for the rapid progress of bronze casting there since high-fire kilns, wheels, and molds for such shapes as the *li* had all previously been developed.[10]

In 1961 Noel Barnard presented detailed and speculative theories of Chinese bronze casting. Following Karlbeck, Barnard takes the position that most decor elements were formed on the pattern rather than the mold surface.[11] More importantly, Barnard introduces his bold concept of "sectionalism"—i.e., building up the total design of a vessel by reproducing the same decor module or section on different parts of the pattern (fig. 6). As he states:

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[8] Terminology in the literature on ancient Chinese bronze casting varies widely and is often inconsistent with modern foundry practice. Terms used in the present paper are defined in the Glossary.

[9] Orvar Karlbeck, "An-yang Moulds," *Bulletin of the Museum of Far Eastern Antiquities*, vol. 7 (1935), pp. 39–60.

[10] Wilma Fairbank, "Piece-mold Craftsmanship and Shang Bronze Design," *Archives of the Chinese Art Society of America*, vol. 16 (1962), pp. 9–15. In 1975 Noel Barnard reiterated this theme in *Metallurgical Remains of Ancient China*, pp. 53–54.

> The importance of the sectional construction of vessel models [patterns] lies not so much in the technique attending the construction of any particular vessel model [pattern] but rather in the further application of the technique throughout specific groups of vessels—i.e., the use of engraved decor blocks [master pattern blocks] (from which decor sections are molded for insertion in to the models [patterns]) throughout vessels manufactured in the same foundry.[12]

This practice, if actually used in producing ancient bronzes, would then make it possible to trace series of vessels from a single foundry. Barnard adds that in the Shang and Western Chou periods this duplication may have been limited to plain, solid relief units; this might be revealed by precise measurement. In late Chou bronzes, however, complete casts of decor elements may have been placed on patterns.[13]

Thus Barnard believes that ancient Chinese foundries may have kept a stock of standard master pattern blocks with surface decor of various dimensions, graduated sizes of flanges, animal heads, handles, and knobs, as well as various patterns in clay replete with grooves and sockets into which various combinations of decor sections could be placed in accordance with the aim of the foundryman or requirements of the patron.[14]

The principle of sectionalism could have been employed in pattern/mold fabrication in two ways. First, molds impressed from fully-decorated partial patterns could be combined to produce a symmetrical total design. This application could be called sectionalism of the mold. On the other hand, use of master pattern blocks bearing a single motif to be replicated without regard to mold division could be called sectionalism of decor.

While Barnard does not clearly distinguish between Shang and Chou techniques, it is doubtful whether either form of sectionalism was used in the Shang period or in the early Western Chou period. A study of four similar *fang-ting*, dating to early Western Chou (one in the Freer Gallery of Art,[15] one in the Hermitage Museum in Norfolk, Virginia, and two in the National Palace Museum in Taipei) was carried out at the Freer Gallery of Art. It was found that the bifurcated serpentine creatures on these vessels are all slightly different and could not have been made by premolding and attachment to the pattern as described by Barnard. In addition, the bosses were apparently punched directly into the mold surface with a single blunt device.[16] However, the concept of sectionalism has great relevance to the study of late Chou bronzes even if it does not appear to hold true for Shang works.

Other scholars have made valuable contributions to the understanding of ancient Chinese foundry practice. R. J. Gettens based his findings on direct examination of the bronzes in the Freer Gallery of Art.[17] Wan Chia-pao, on the other hand, has experimented with making bronze castings in the ancient manner,[18] while Cyril Smith derives some of his ideas from contemporary Japanese art foundry practice.[19]

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[11] Noel Barnard, *Bronze Casting and Bronze Alloys in Ancient China* (Canberra: Australian National University, 1961), pp. 73–74.

[12] *Ibid.*, p. 75. Terms in brackets are those used by the present author.

[13] *Ibid.*

[14] *Ibid.*, p. 126.

[15] Pope, *et al.*, *The Freer Chinese Bronzes*, vol. 1, p. 190.

[16] W. T. Chase, private communication.

In 1972 Smith emphasized the idea of producing decor directly in the mold surface. He asserts that the unique character of Chinese bronzes results from the surface of the bronze being a direct replica of the surface shaped by the artist without repeated inversions in materials of different textures and plasticities.[20] When it was first discovered that Chinese bronzes were cast in piece molds, some scholars were quick to point out that single mold sections, extended around curved surfaces, carry details protruding at angles that could not draw without damage. They questioned how such molds were made, as it was most unlikely that a flexible molding material could have been used in ancient China. A possible solution may be found in the casting of temple bells at the Takahashi Foundry in Kyoto or the casting of hibachi at the Enjo Foundry in Matsue, Japan. Neither of these foundries uses three-dimensional patterns; rather, a cavity—i.e., the negative of the form to be produced, is utilized. It is generated directly in space and the decoration impressed with metal loose pieces shaped to match the curvature of the mold, directly in the mold surface. Withdrawal of the mold from the pattern presents no problem, as there is no full pattern; and the loose pieces are small enough to be withdrawn in a direction normal to the local surface.[21]

Smith does not suggest that molds for all Chinese bronzes were swept out rather than formed over smooth patterns, although most shapes would lend themselves to such treatment. It does seem to him that the mold divisions were needed as much for providing access to the surface for decoration as for removal from the pattern. In Shang bronzes major elements in medium relief may have been stamped into the fresh surface of the mold (a mask from An-yang appears to be such a stamp) and the *lei-wen* meanders carved into the mold when it reached the proper degree of hardness. Later bronzes, he notes, depend to a greater extent on the mechanical replication of decor, but he believes it is a mistake to conclude that all bronzes of a period were made by the same technique.[22]

The accounts summarized above are concerned primarily with Shang casting techniques; their common points underscore the unique character of this technical tradition. Most notable is the intimate relationship between ceramic and metallurgical processes as reflected in the use of piece molding rather than the *cire-perdue* technique. Related to this issue is the degree to which the pattern was decorated and designs transferred to the mold from the pattern and the degree to which the mold surface itself was decorated.

More recently, the ways in which this technical tradition was modified in the late Chou period have received attention, and sharper distinctions between Shang and Chou foundry practices have been drawn. Here published material from the Chinese excavations at the late Chou foundry site at Hou-ma has been helpful.[23] In addition, Gettens has analyzed the interlock casting of vessels and appendages characteristic of the Chou period,[24] and a previous study of the Freer and Minneapolis *chien* proved conclusively that identical decor motifs were present on both members of the pair—a technique apparently unprecedented in the Shang period.[25] Still more recently, Wan Chia-pao studied the casting of Shang and Chou *ting*; his conclusion relates closely to Barnard's concept of sectionalism.

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[17] Rutherford J. Gettens, *The Freer Chinese Bronzes*, vol. 2 (Washington, D.C.: Smithsonian Institution, 1964).

[18] Li Chi and Wan Chia-pao, *Studies of the Bronze Ku-beaker*, (Taipei: Academia Sinica, 1964).

[19] Cyril S. Smith, "Metallurgical Footnotes to the History of Art," *Proceedings of the American Philosophical Society*, Vol. 116 (1972), pp. 108–114. Also, Japanese art foundry practice is documented in a film, "The Enjo Foundry," by Robert E. Debold and Edward W. Yates, produced with a grant from the Desert Research Institute, Reno, Nevada.

[20] Smith, "Metallurgical Footnotes," p. 112.

[21] *Ibid.*, pp. 108–111.

[22] *Ibid.*, pp. 111–112.

> [In the late Chou period] the universal application of the casting-on method, the separate casting of the various appendages, the possibilities of alternative usage of ready-made parts, the duplication of decor in one or more vessels by stamping (i.e. use of master pattern [blocks]) are all aspects of an advanced form of mass production.[26]

By 1975 Barnard himself was citing evidence from Hou-ma foundry remains to support his theory of sectionalism. Fully decorated patterns for appendages, he states, were used to prepare molds which could either be used directly for casting in bronze, or used for casting "duplicate models" [patterns]. Duplicate patterns in turn may have been used to produce duplicate or "second generation" molds for casting legs and handles of nearly identical size and shape for incorporation in interlock castings of various vessels or series of vessels. To support this theory Barnard points to Hou-ma pattern fragments with mold marks indicating they were cast in slip. Further, he notes fragments from Hou-ma which appear to be master pattern blocks, as they are flat slabs of clay, each incorporating a complete decor motif in all its detail, sculpted in the positive (fig. 7). Thus, as Smith had suggested, clay impressions in the negative could be incorporated directly into the mold surface. Barnard mentions a Hou-ma mold fragment for a bell which contains pre-molded insets and thus provides direct evidence that this technique was indeed practiced in the late Chou period.[27]

Thus an additional modification of casting technique in the Chou period appears to be a shift from placing decor on the pattern and incising only details in the mold, to decorating the mold surface directly. Nevertheless, several aspects of late Chou bronze casting technique remain to be clarified. To what

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[23] Chang Han, "*Hou-ma Tung-Chou i-chih chu-t'ung tao-fan hua-wen so-chien*," ("On the design of the molds for casting the bronze which were discovered at Hou-ma in the Eastern Chou sites"), *Wen-wu*, no. 10 (1961), pp. 31–34. Unpublished translation from the Chinese by Takashi Katsuki. Chang Shou-chung, "*1959 nien Hou-ma* 'Niu-ts'un ku-ch'eng' *nan tung Chou i-chih fa-chüeh chien-pao*" ("A brief report on the excavation of the Eastern Chou sites in 1959, south of 'Niu-ts'un ku-ch'eng' in Hou-ma City"), *Wen-wu*, no. 8–9 (1960), pp. 11–14. Unpublished translation from the Chinese by Takashi Katsuki. Chang Wan-chung, "*Hou-ma Tung-Chou tao-fan ti tsao-hsing kung-i*" ("The plastic art of the Eastern Chou clay molds discovered at Hou-ma, Shansi"), *Wen-wu*, no. 4–5 (1962), pp. 37–42. Unpublished translation from the Chinese by Takashi Katsuki. Page references in subsequent footnotes are to these translations at the Freer Gallery of Art. These articles are discussed by Noel Barnard and Sāto Tamotsu in *Metallurgical Remains of Ancient China* (Tokyo: Nichiōshen, 1975), pp. 54–60; and also in Part IV of the present paper.

[24] Gettens, *The Freer Chinese Bronzes*, vol. 2, pp. 76–86.

[25] Keyser, "A Technical Study," pp. 52–54.

[26] Wan Chia-pao, "A Comparative Study of the Casting of Bronze *Ting*," p. 43.

[27] Barnard, *Metallurgical Remains*, pp. 57–58.

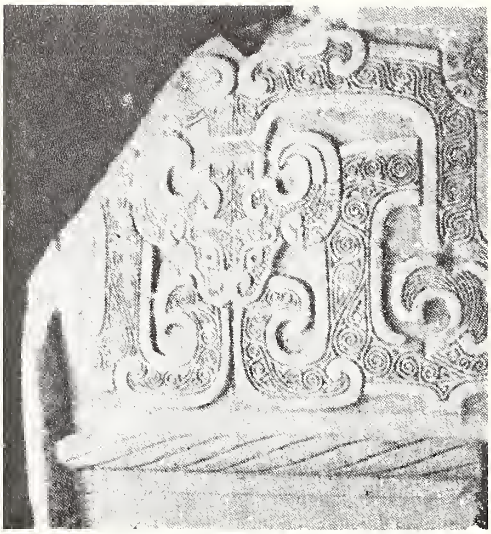

FIG. 7.—Fragment from Hou-ma (after *Wen-wu*, no. 10 (1961), Figure 5.)

extent were late Chou bronzes designed in a modular way? Is sectionalism in the pattern/mold involved, or merely sectionalism of individual decor motifs? In either case, exactly how were designs built up from their smaller units? Were decor units always placed directly in the mold surface? Were appendages indeed cast from identical molds (either "first" or "second" generation), and were there additional ways of attaching them to the vessels?

TECHNICAL DESCRIPTION OF THE PAIR OF *CHIEN*

The *chien* were examined several times, both separately and together. Both raking illumination and ultraviolet light were used. Measurements were made and compared using calipers. In addition, the Freer Gallery of Art provided detail photographs and radiographs of the two vessels for study.[28]

CONDITION

According to wet chemical analysis performed at the Freer Gallery of Art from samples taken from the foot rims of the two *chien*, the vessels are very similar in composition: the Freer *chien* is 70.8% copper, 12.8% tin, 14.7% lead, and 0.1% iron for a total of 98.3%; and the Minneapolis vessel is 72.2% copper, 12.1% tin, 14.4% lead and 0.3% iron for a total of 99.0%.[29] In addition, the composition of a handle of the Freer *chien* is very close to that of the body (69.2% copper, 14.3% tin, 14.2% lead, total 97.7%) indicating that metal from the same melt could have been used to produce both.[30]

Both bronzes are covered with a compact, pale-green corrosion product, probably tin oxide. Green malachite-like granules are scattered over the surface, and small areas of a red corrosion product, probably cuprite, are also apparent. A blue azurite-like substance as well as unidentified white and black corrosion products appear on the bottom of the vessels within the foot rim. The inside surfaces of both vessels have a grayish, metallic appearance. On both *chien* an encrustation of malachite runs around the inside circumference of the vessels about 5 cm below the rim; possibly this marks a line where water stood in the vessels over a period of time. Above this line the layer of malachite and azurite becomes thicker and appears as a uniform granular encrustation. Compact deposits of reddish earth appear inside the vessels, while harder reddish-buff accretions inside the foot may be core material. Both vessels appear mechanically sound and their patinas stable.

The only defects or repairs in either vessel are cracks in the upper portion of one of the handles of the Minneapolis *chien*. In addition, the join between the lower portion of another handle on the same vessel fluoresces orange under ultraviolet light and may therefore be a modern repair.

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[28] Since the original radiographs are quite large, the reproductions of them shown here necessarily render detailed study difficult.

[29] Freer Gallery of Art examination records.

[30] Pope, *et al.*, *The Freer Chinese Bronzes*, vol. 1, p. 483.

FABRICATION DETAILS

Dimensions

The Freer *chien* has a diameter of 43.8 cm measured at the plain handles and is 22.4 cm high. The Minneapolis *chien* has a diameter of 43.85 cm at the plain handles and is also 22.4 cm high.

Mold Marks

Both *chien* display four vertical mold marks dividing them into quarters at the handles (figs. 1 and 2); this indicates that they were cast in four-piece molds. The mold marks are discernible all the way from the foot to the rim of the vessels except in the undecorated area between the lowest decor band and the foot, where they were probably removed in the process of post-casting finishing. No horizontal joins are evident. Most of the vertical joins have slipped slightly in casting and are readily visible.

Casting Remnants

Both vessels bear casting remnants approximately in the center of the area within the foot (arrow 1, fig. 8), indicating that they were cast in an inverted position. That of the Freer *chien* is 6.35 cm long, 0.3 cm high, and is oriented at about a 60° angle from an axis drawn across the ringed handles. That of the Minneapolis *chien* is 3.8 cm long, 0.5 cm high, and is oriented at a 45° angle to the same axis.[31]

Casting Irregularities

Radiographs of the Freer *chien* reveal considerable porosity in the undecorated area and bottom of the vessel. Thicker ridges of metal radiate inward from the foot (arrow 2, fig. 8); these may have formed when the metal shrank on cooling, as there would be space between the metal and the top of the mold assembly. Or, as Gettens suggests, metal may have seeped into cracks in the mold.[32] The thickness of the metal is fairly uniform, though some variation does appear. An interesting irregularity appears in the lowest decor band in the upper right quadrant of the radiograph of the Freer *chien* (arrow 3, fig. 8). Here an area of thicker metal runs halfway up the band through nearly the entire quadrant. While this defect may have occurred as the design was stamped into the clay, it could also have occurred if the mold assembly shifted slightly during the casting process. Or, as Williams suggests, this line may be a "hot tear" resulting from stress in the metal during cooling. He notes that such tears are common on the outside surfaces of round castings made with copper-based alloys.[33]

Porosity and ridges of metal in the foot of the Minneapolis *chien* are similar to those of the Freer vessel. Radiographs show that on

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[31] Dr. Douglas C. Williams of the Department of Metallurgical Engineering at The Ohio State University at Columbus believes the narrow opening of this casting remnant would not have permitted a flow of metal rapid enough to fill the mold properly. He believes the gates for casting may have been located on the foot rims of the bronzes and that the remnant seen is an air vent.

[32] Pope, *et al.*, *The Freer Chinese Bronzes*, vol. 1, p. 481.

[33] Williams, private communication.

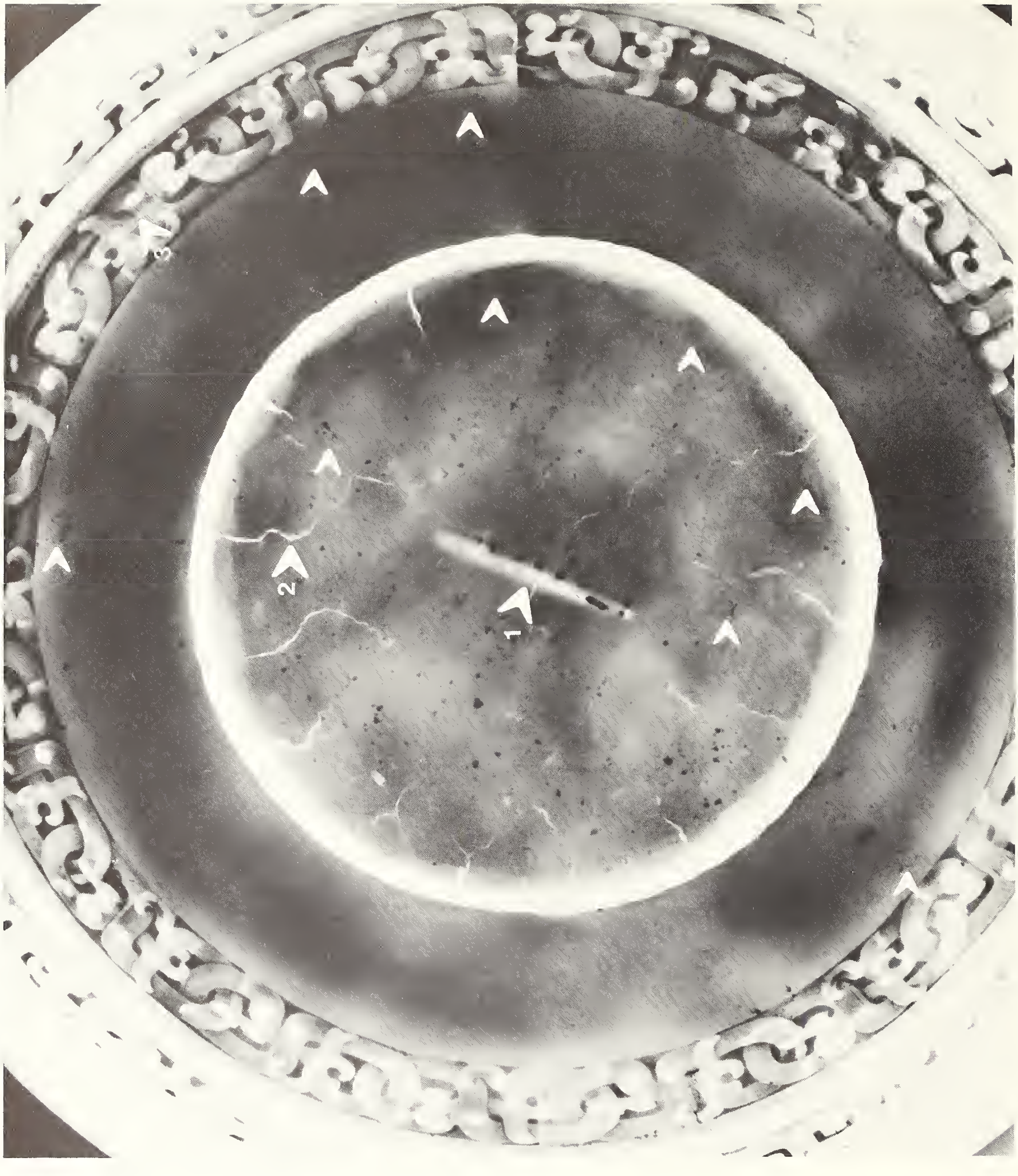

Fig. 8.—Radiograph of the Freer *chien*, base down on film.

the Minneapolis bronze the metal is noticeably thicker in one quadrant of the undecorated area than the other three, whereas on the Freer vessel the irregularities in thickness are more uniformly distributed among the four mold divisions. The Minneapolis *chien* displays no hot tears.

Chaplets

Most of the chaplets (alternatively termed spacers) on both *chien* are all but invisible when examined with the naked eye but are revealed in the radiographs. On the Freer vessel, there are chaplets at each end of the casting remnant (small unnumbered arrows, fig. 8). Three others, less distinct, are distributed in a semicircle in the lower right quadrant of the vessel near the foot. There are four chaplets in the undecorated area, three in the upper right quadrant on Figure 8 and one in the lower left. All are near the lowest decor band. One chaplet is definitely discernible in the lowest decor band itself; it is near the mold join at the right. There are numerous chaplets in the raised area between the middle and the lowest decor bands; several of these have edges running under the braid. They also occur at intervals in the middle decor band, and some of these also have edges running under the raised areas of decor (fig. 9). Chaplets on the interval between the top and middle bands resemble those on the other such areas: those visible in Figure 9 are on the lower side of the braid and some run partly under it. Numerous chaplets appear in the top decor band as well. They are usually placed in the flat areas of the design, but their edges do run under the raised areas.

The Minneapolis *chien* has six chaplets within the foot—one at each end of the casting remnant and three near the foot ring. There are six chaplets in the undecorated area; most are near the lower decor band. Again, there are few chaplets on the lowest decor band. The one which is clearly discernible is placed on a flat area and does not run under the design. Two chaplets are visible on a radiograph in the section between the lower and middle bands, one above and one below the braid; the lower one intersects the braid. Several chaplets appear in the middle band; all are placed in flat areas of the design, and only one runs under the raised bands. There are numerous chaplets on the area between the middle and upper decor bands both above and below the braid. None intersects the braid. A few chaplets are discernible in flat areas in the upper band. Thus the arrangement of chaplets is similar, though not identical, on both *chien*.

Handle Assembly

All four handles on each *chien* are separately cast with ceramic cores. The heads and stems were cast together and no mold marks or seams are visible. Striations on the flat sides of the stems may be file marks, however. In addition, a line of hard solder running around each join between the handle and the body indicates that the handles were brazed onto the vessel bodies after casting.[34]

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[34] Gettens states that this type of solder was a copper-lead-tin alloy with a much higher tin content than the alloy of the handle and vessel to give it a lower melting point. He cites Herbert Maryon, who says that separate parts made of copper and its alloys cannot be joined simply by heating to incipient fusion or by hammering because of the formation of a film of copper oxide on their surfaces. Except for such mechanical joining techniques as riveting or casting-on, copper alloys can only be joined with a hard or soft solder with a melting point lower than the points

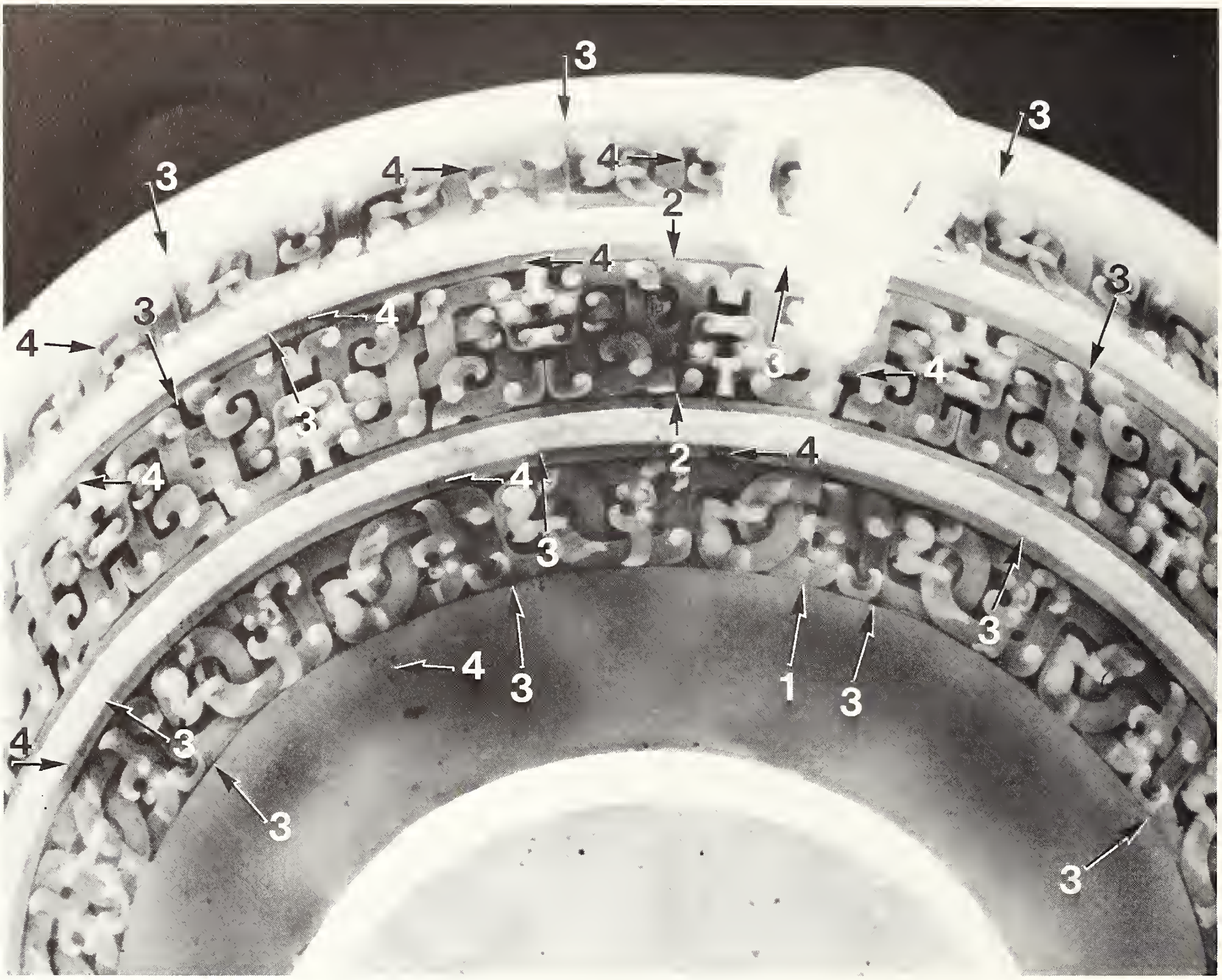

Fig. 9.—Radiograph of the Freer *chien*, inscription down on film. 1. Mold join; 2. Major join in motif; 3. Motif join; 4. Chaplet.

As Noel Barnard states in his examination notes on the Freer vessel, each handle has a small hole near the join, with a small blob of solder over it. As it seems unlikely that these are inlets for the joining metal, he suggests that they are a locking device.[35] In addition, radiographs of the Minneapolis *chien* reveal bosses which were cast with the vessel to receive the handles and thus reinforce the soldered join (arrows, fig. 10).

The rings on the vessels' handles are cast solid. They show no sign of a join and were undoubtedly added before the handles were brazed on. Fine parallel striations on their reverse sides may be file marks.

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to be joined. The contact surfaces must be very clean and freed from oxides with acids or fluxes so that the soldering can wet the surfaces. Gettens adds that the Chinese must have used some sort of flux for brazing, but what it was is completely unknown. Gettens, *The Freer Chinese Bronzes*, vol. 2, pp. 84–86.

[35] Freer Gallery of Art Examination records.

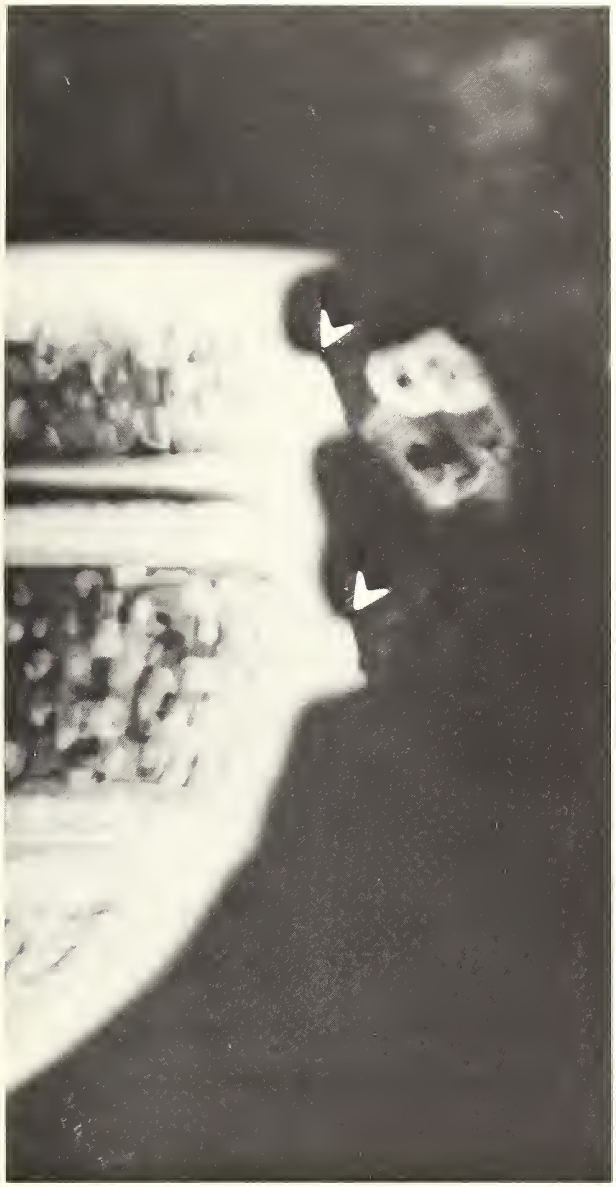

FIG. 10.—Radiograph of a handle of the Minneapolis *chien*.

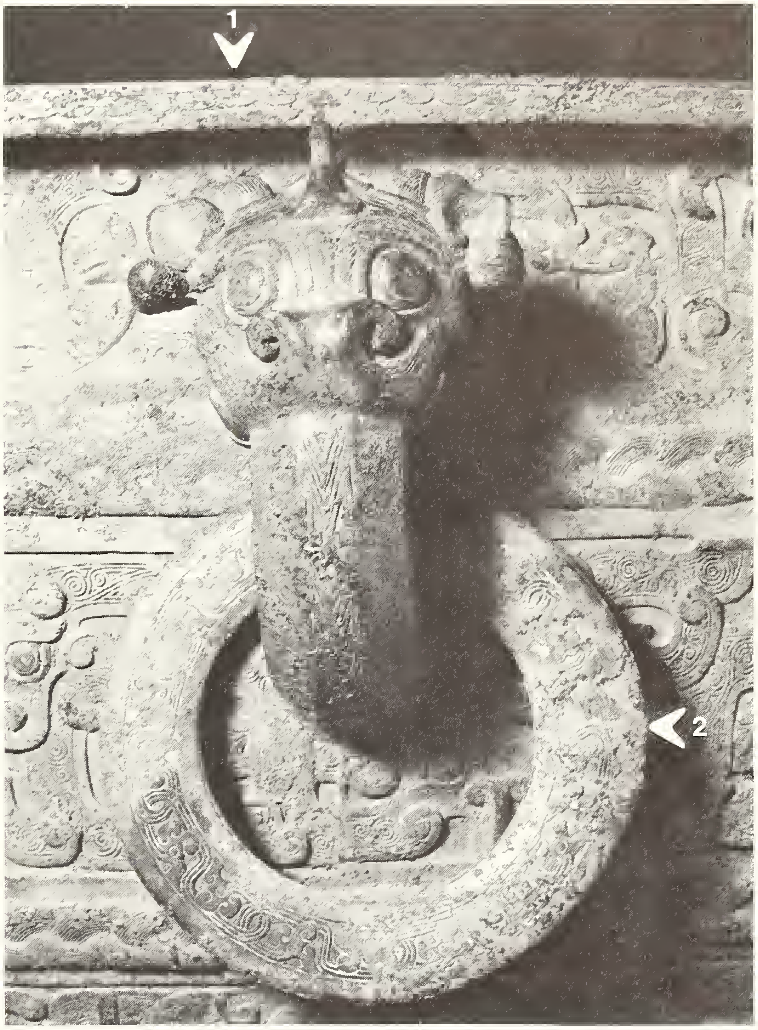

FIG. 11.—Handle of the Freer *chien*.

DECOR REPLICATION

Decor on Rims of Vessels

As mentioned above, the decor here consists of interlocking two-headed creatures with ribbon bodies, each 3.4 cm long; this band of decor is 1.0 cm wide. On the Freer *chien*, the motif begins just to the left of the handle with the bulging ring (arrow 1, fig. 11), where the presence of three, rather than two, consecutive body bands indicates a major join in the motif (arrow, fig. 12). Each unit of repetition consists of four complete creatures and is 10.4 cm long (fig. 13); ridges on the interlocking body bands in the location indicated in Figure 13 mark the joins on the motif. Proceeding to the viewer's right from the major join, the motif repeats twelve times and finishes with a partial section 7 cm long.

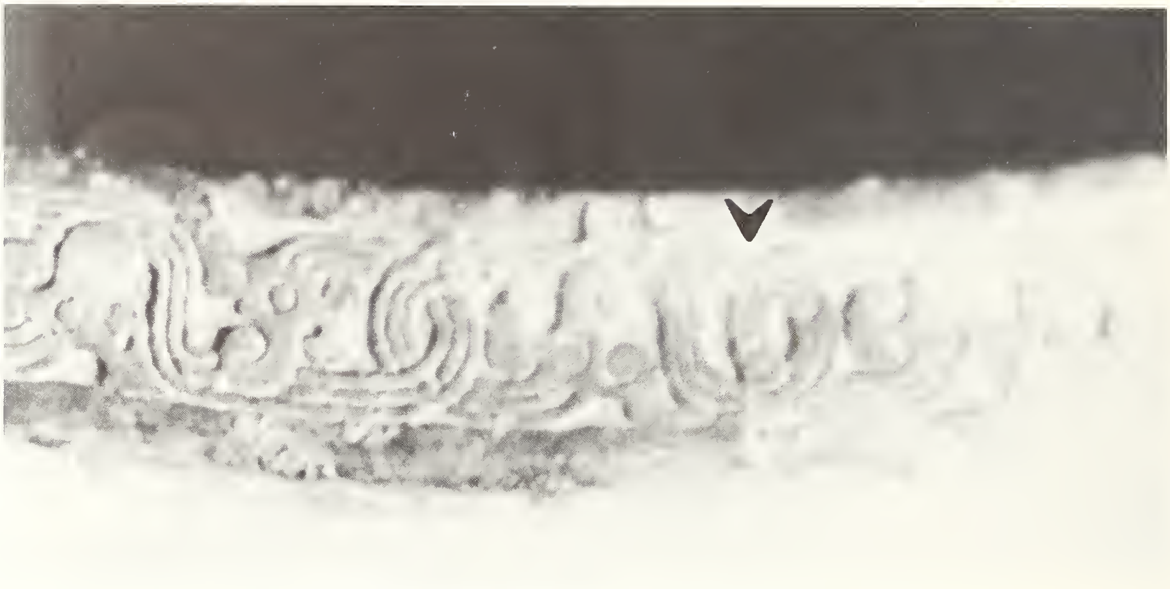

Fig. 12.—Major join of motif on the rim of the Freer *chien* (× 3).

The decor on the Minneapolis *chien* is replicated in the same way as that of the Freer vessel. Starting near the handle on the Minneapolis *chien* (arrow 1, fig. 14), it repeats twelve times and has a finishing section 7.0 cm long. Here too the band of decor is 1.0 cm wide, each creature is 3.4 cm long, and the unit of replication consists of four creatures and is 10.4 cm long.

Decor on Rings

The rings on the vessels' handles bear interlaced creatures like those on the rim (arrow 2, fig. 11). The motif on the Freer vessel is 0.8 cm wide, and the individual creatures are 3.0 cm long. There are nine of them on each ring with no sign of a join; one master pattern block was apparently used to produce the entire decor on the ring.

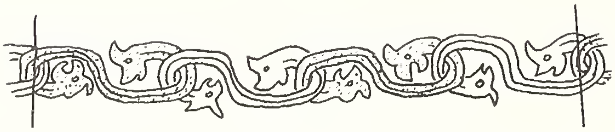

Fig. 13.—Motif from the rim of the *chien*, showing the location of joins.

The decor on the rings of the Minneapolis *chien* is like that of its mate: there are nine interlocked creatures of the same dimensions on each ring, and, again, there is no sign of a join in the decor.

Cowrie Decor

Each vessel displays a row of cowries on its rim. On the Freer *chien* this band is 0.38 cm wide and each cowrie about 0.6 cm long. This motif starts just to the viewer's right of the handle where a ridge of metal indicating a join in the motif is visible in raking light (arrow 1, fig. 15). Proceeding to the viewer's right, joins are at intervals of 14.5 cm; each embraces twenty-four cowries. This unit is repeated nine times, with a 5.3 cm section

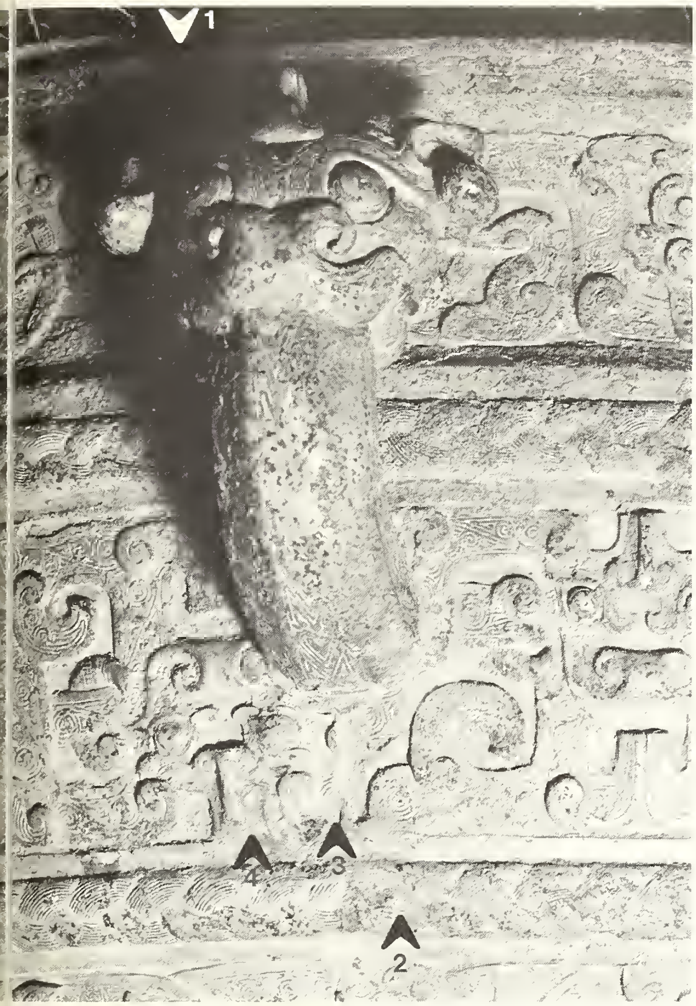

Fig. 14.—Detail photograph of the Minneapolis *chien*.

added to complete the circumference of the vessel.

On the Minneapolis *chien* the cowries have the same dimensions as those on the other vessel, but there is more irregularity in the units of repetition. This motif starts 11.8 cm to the viewer's left of the handle where there is an irregularity of register in the cowries (arrow, fig. 16). Moving to the right, there are four units 14.5 cm long with twenty-four shells as on the Freer vessel, one with twenty-three (13.86 cm long), two with twenty-four, another with twenty-three, and two irregular strips with fourteen (8.96 cm long) and nineteen cowries (12.2 cm long) respectively.

Braid Decor

Top band. On the Freer *chien* this band of plait decor is 1.2 cm wide. The motif starts just to the viewer's right of the handle (arrow 2, fig. 15), where a doubled section indicates a major join. Proceeding from this point to the viewer's right, joins are discernible either as ridges, pinched areas, or depressions at intervals of 17 cm. This unit is repeated seven times with an odd section 13.3 cm long to complete the band of decor.

The top band of braid decor is also 1.2 cm wide on the Minneapolis *chien*, but again there is greater variation in the units of repetition. Starting at the viewer's left of the handle (arrow 1, fig. 17) and proceeding to the right, the first motif unit is 17 cm long, followed by one 19 cm long, one 15.4 cm long, four 17 cm long, and a final section 14 cm long.

Lower band. On the Freer vessel this band of plait decor is also 1.2 cm wide. Starting just to the left of the handle (arrow, fig. 18), the motif joins are evident at 17 cm intervals as before. There are six of these units plus odd segments of 15 and 5.3 cm.

The lower band of braid is also 1.2 cm wide on the Minneapolis *chien*. Starting below the handle just to the viewer's right of the mold join (arrow 2, fig. 14), the first segment is 17 cm long, followed by sections 16.5 cm, 17 cm, 14.5 cm, 17 cm, 16.5 cm, 17 cm, and last 7 cm long. Thus, as on the top band of braid, the basic unit of repetition is

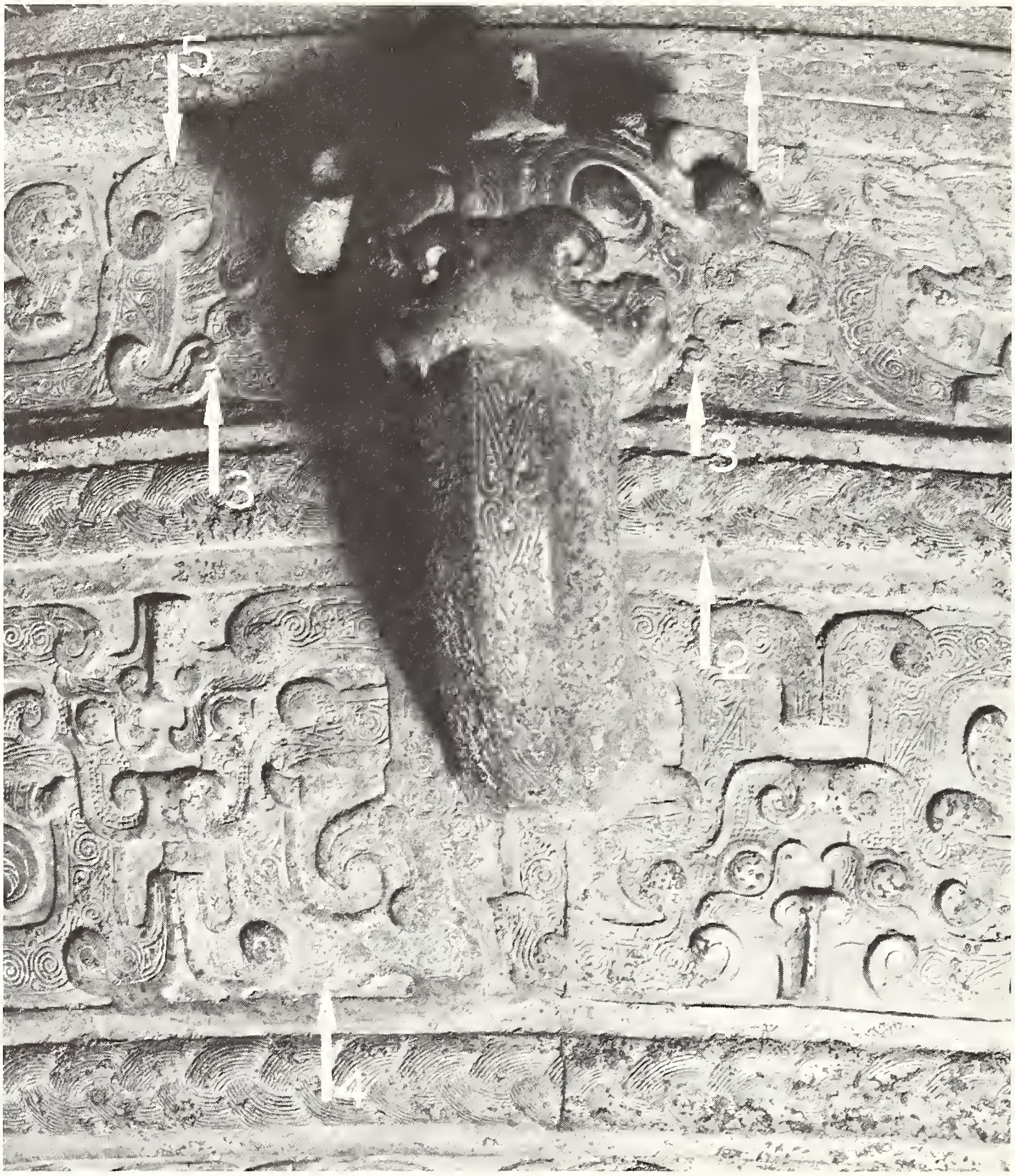

Fig. 15.—Detail photograph of the Freer *chien*.

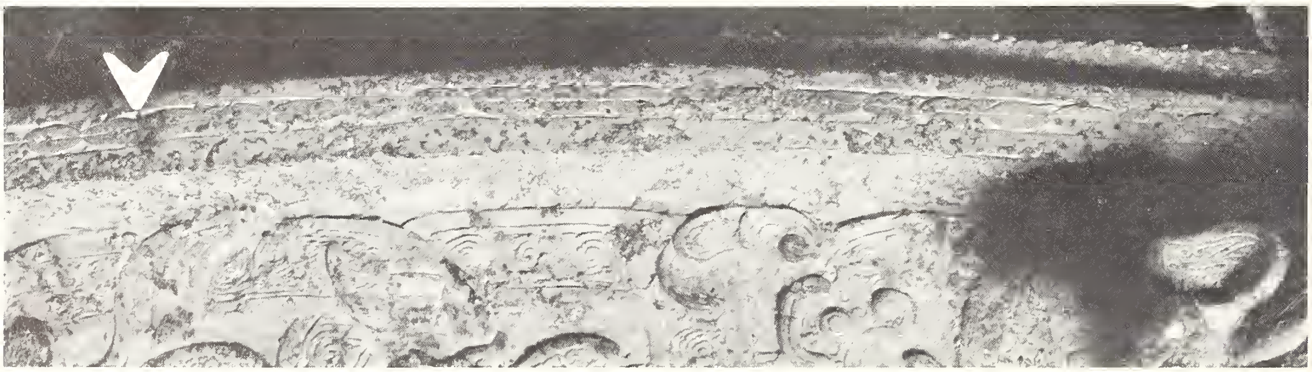

Fig. 16.—Detail photograph of the Minneapolis *chien*.

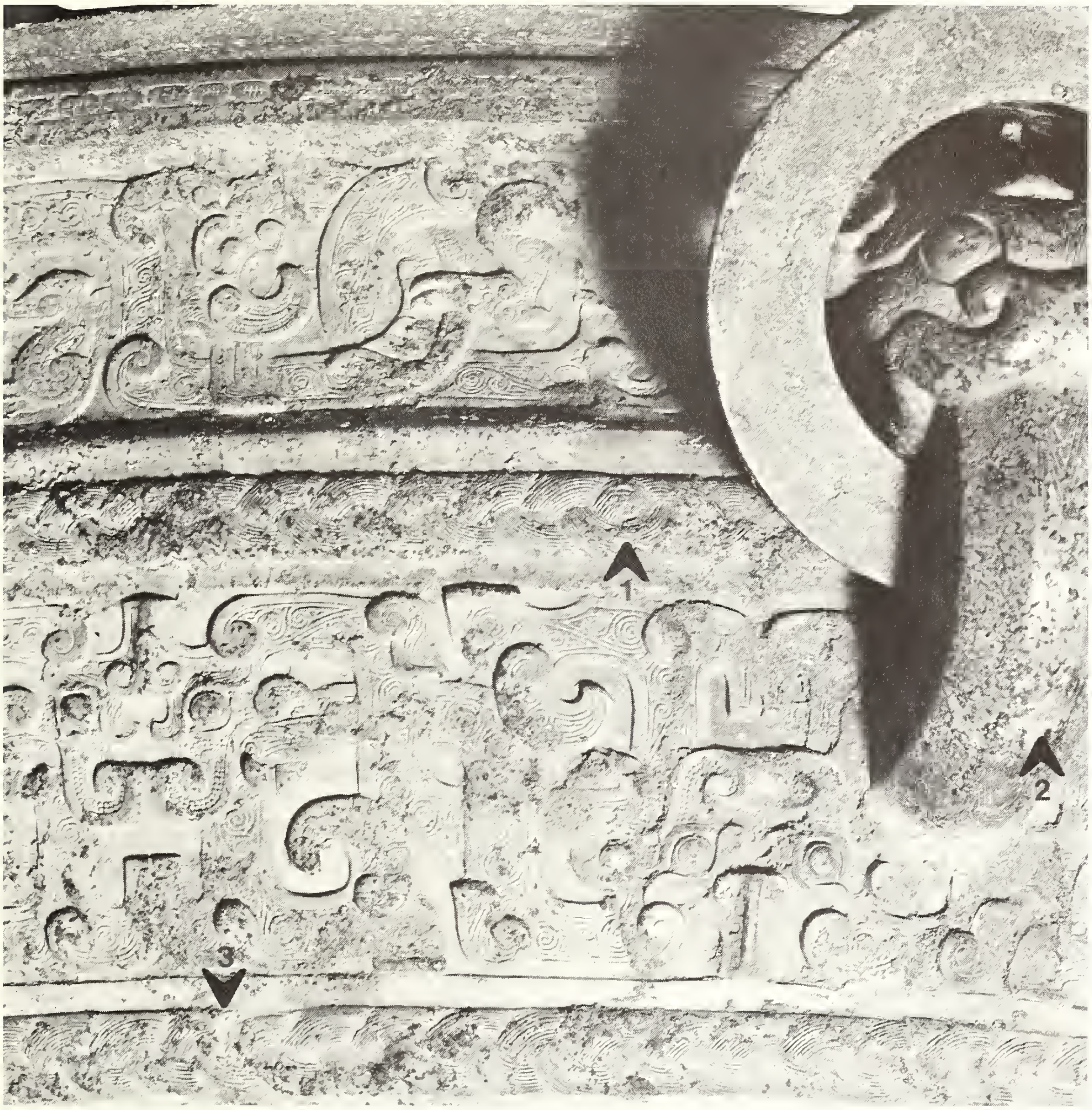

FIG. 17.—Detail photograph of the Minneapolis *chien*.

17 cm but varies more on the Minneapolis vessel than on the Freer vessel.

Braid on foot. On the Freer vessel this decor band is 2.1 cm wide and begins with a very marked major join (arrow, fig. 19). The units are less regular in length than those on the upper bands of braid: proceeding to the viewer's right from the major join, the first segment is 13.3 cm long; the second, 11.5 cm; the third, 13.0 cm; then segments 13.2 and 11.5 cm long plus a finishing section 6 cm long. It is interesting to note that the direction of the braid in this finishing section is contrary to that of the rest of the plait in this band.

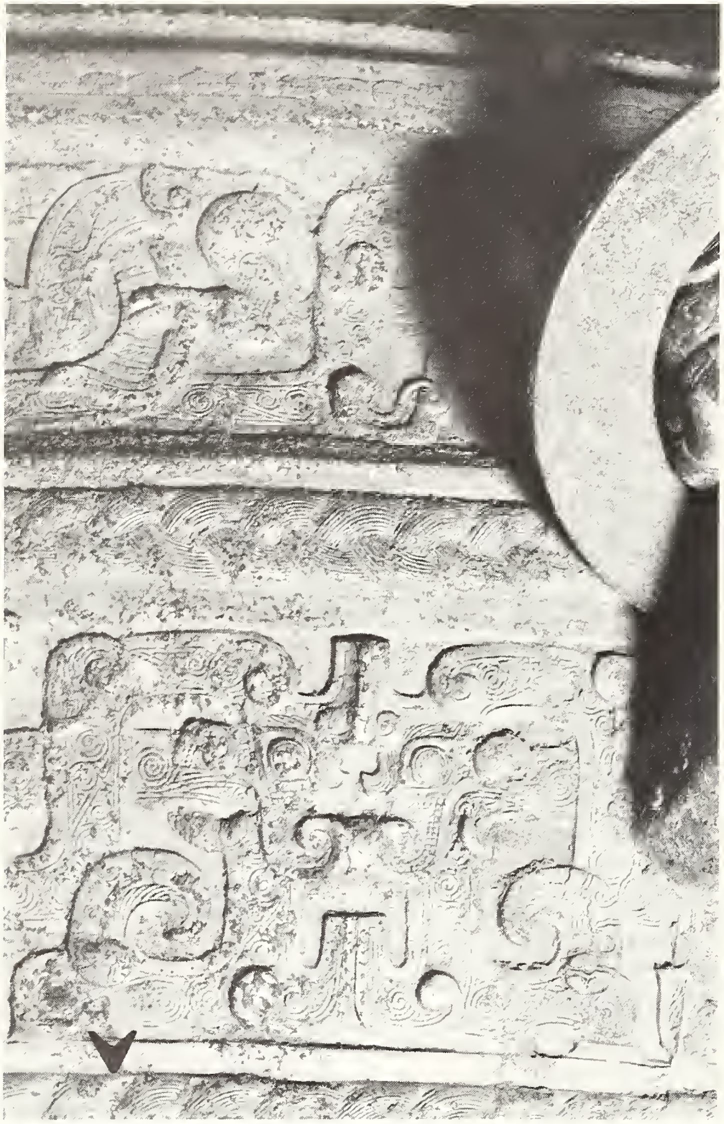

Fig. 18.—Detail photograph of the Freer *chien.*

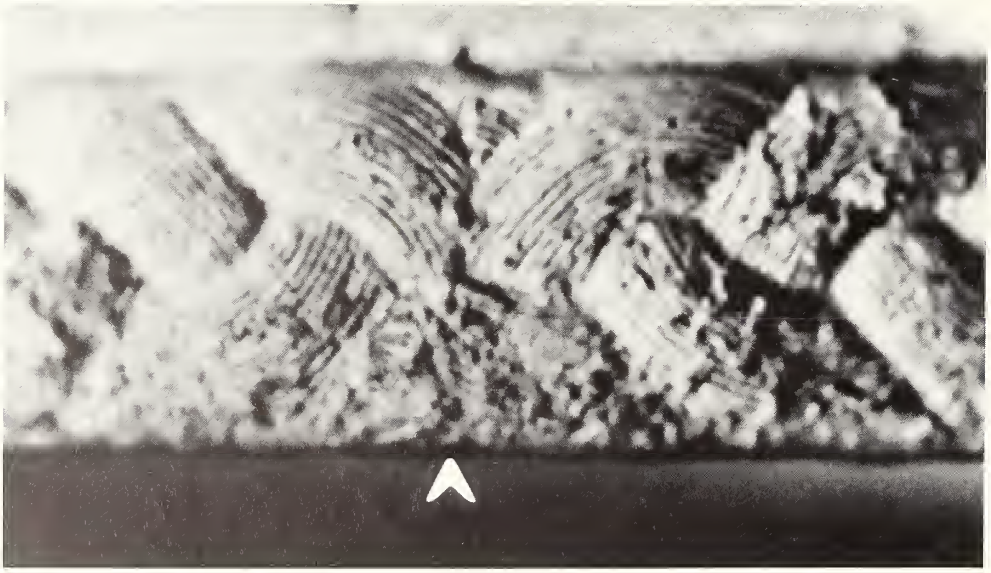

Fig. 19.—Major join of braid on the foot of the Freer *chien.* (×3)

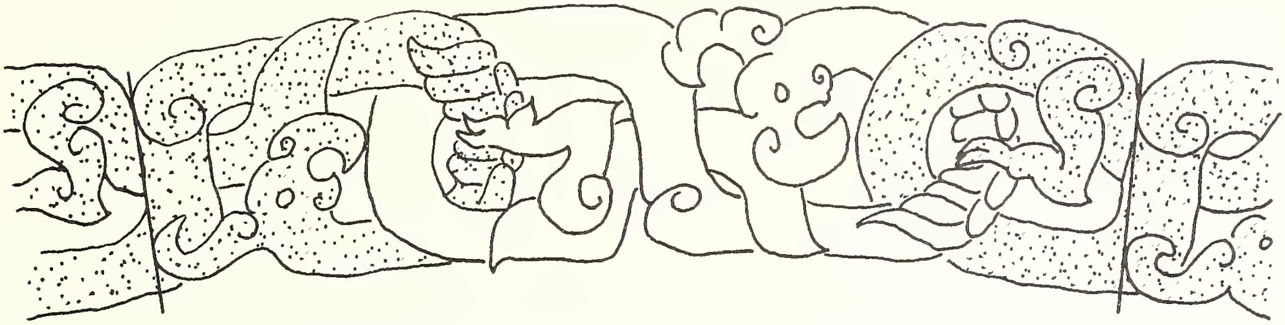

Fig. 20.—Bird-dragon motif from the *chien*, showing the location of joins.

The braid on the foot of the Minneapolis vessel is also 2.1 cm wide. Starting at a point just to the viewer's right of the mold join, pattern joins are discernible at regular 13 cm intervals. This unit is repeated five times with a finishing section 5.0 cm long.

Bird-Dragon Decor.

Upper band. This band on the Freer *chien* is 3.75 cm high, measured from the ridges on either side of the zoomorphs. The major join of this decor band is hidden by the handle in Figure 15; here two inverted creatures appear together as there is insufficient space to place the complete motif (arrow 3, fig. 15). Starting at this point and proceeding to the viewer's right, the design repeats 9¼ times. The motif joins are discernible on close examination: they occur between the leg and descending body band of each inverted bird-dragon; the upright creatures are uninterrupted (fig. 20). The motif joins are marked by discontinuity of planes, thickness of the boundary lines on the body bands, and evidence of hand retouching. The complete motif is 13.5 cm long.

The upper band of bird-dragon decor on the Minneapolis *chien* is also 3.75 cm high. The major join resembles that of the Freer vessel as it is concealed by a handle. The motif joins are like those of the Freer bronze (arrow, fig. 21), and the motif also repeats 9¼ times at intervals averaging 13.5 cm.

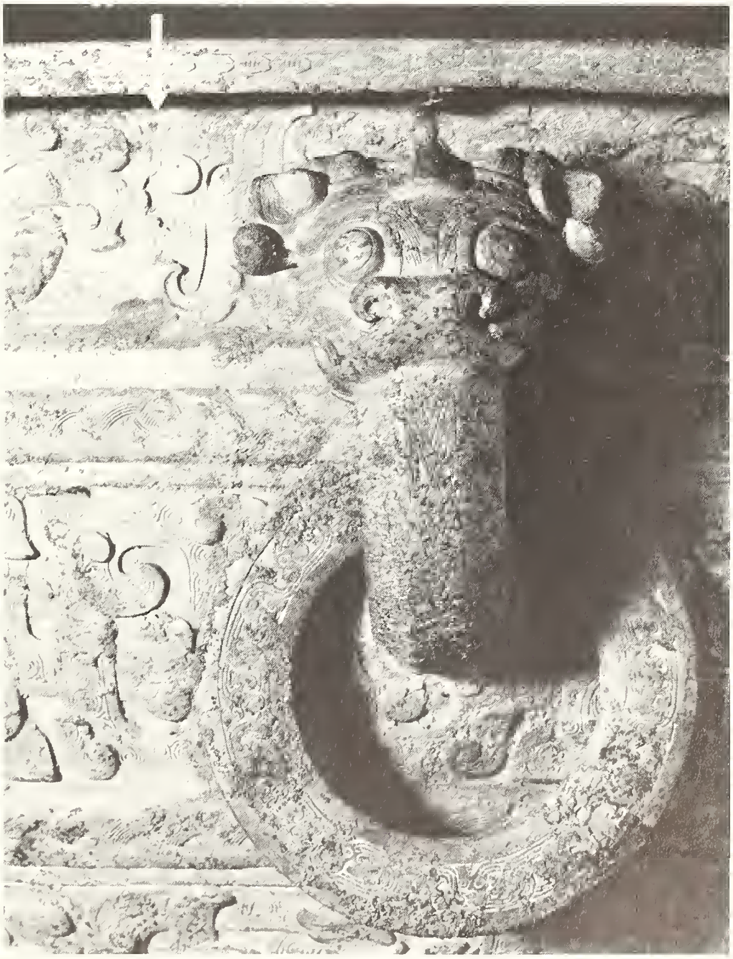

Fig. 21.—Handle of the Minneapolis *chien*.

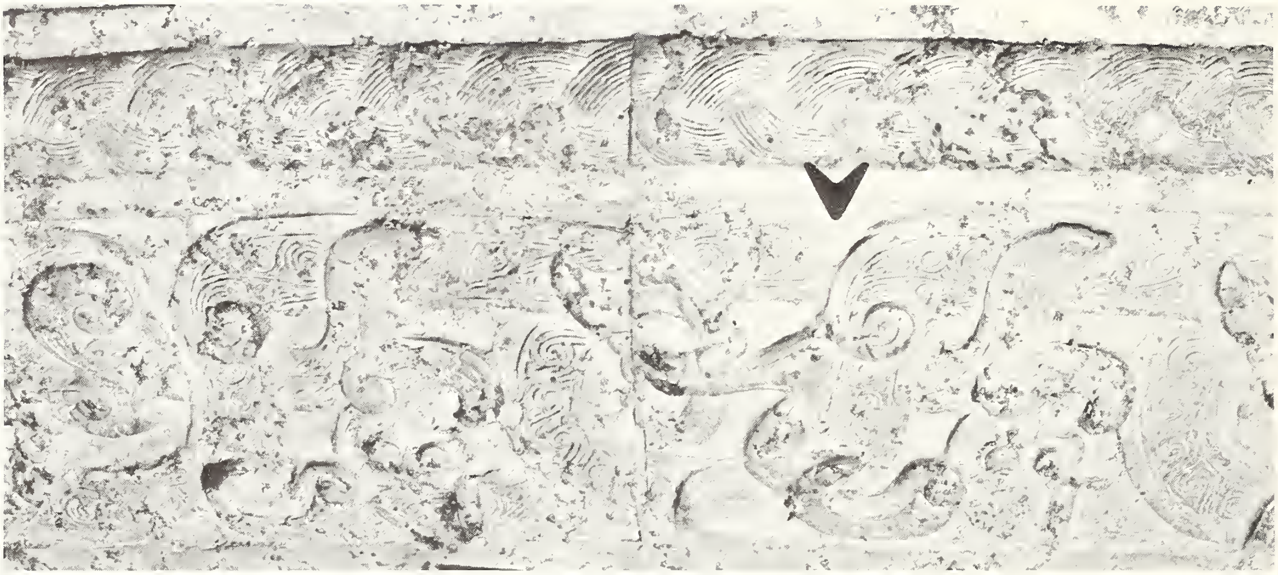

Fig. 22.—Detail photograph of the Freer *chien*.

Lower band. This decor band on the Freer *chien* is 3.75 cm high like the top band. Two inverted bird-dragons appear together at the major join (arrow, fig. 22). The motif begins at the viewer's left and proceeds to the right; it is repeated $8\frac{1}{4}$ times at average intervals of 12.8 cm and runs uninterruptedly around the vessel regardless of the mold joins. The motif joins show up well on the radiographs (fig. 9); they occur in exactly the same point in the motif as on the top band.

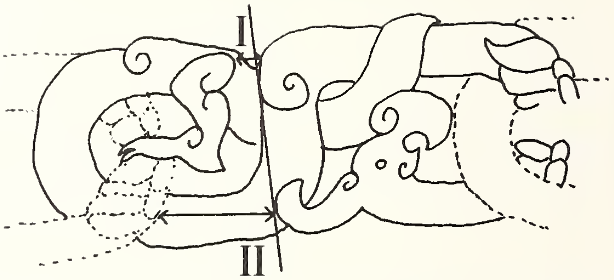

Fig. 23.—Locations of measurements of the bird-dragon motif from the Freer *chien*.

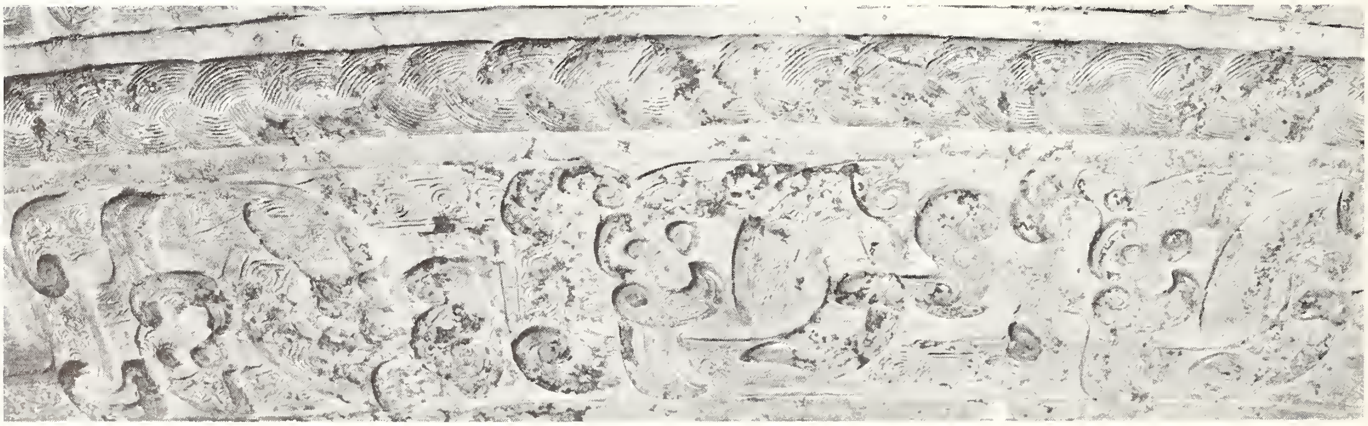

Fig. 24.—Detail photograph of the Minneapolis *chien*.

Careful comparison and superimposition of transparencies of the upper and lower decor bands indicate that the motif is identical in every detail. Measuring the gaps at the motif joins accounts for the 0.7 cm discrepancy in the motif's overall length. The length of the motif in the upper band, measured from the curl of the inverted bird-dragon's leg to that of the next inverted bird-dragon (fig. 23), is 13.4 cm; the same measurement on the lower band is 13.3 cm, a difference of 0.1 cm. The interval I in Figure 23 measures 0.4 cm on the top band and 0.3 cm on the lower band. This difference, 0.1 cm, accounts for the discrepancy. More importantly, the motif in the upper band, measured from one descending body band of the inverted bird-dragon to the next is 13.5 cm. The same measurement on the lower band is 12.8 cm. However, interval II on Figure 23 measures 3.2 cm on the upper band and 2.5 cm on the lower one. Thus the difference of 0.7 cm accounts for this discrepancy also.

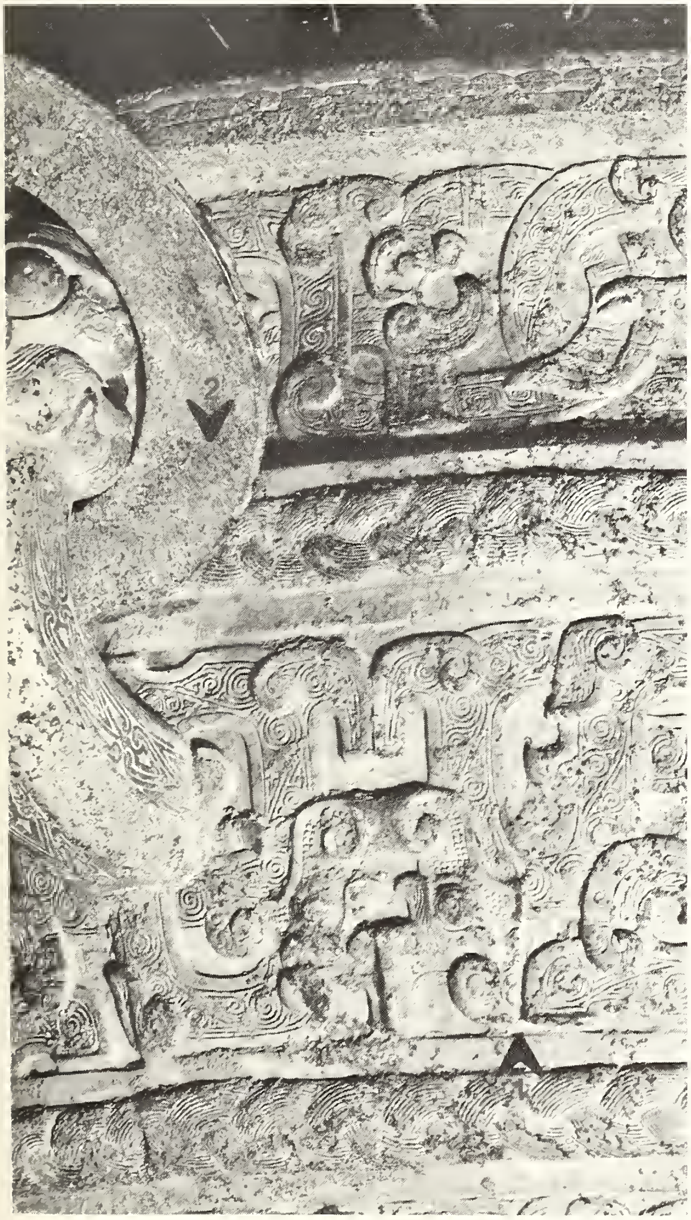

Fig. 25.—Detail photograph of the Freer *chien*.

The lower band of bird-dragon decor on the Minneapolis *chien* is also 3.75 cm high. The major join (arrow, fig. 24), occurs where two upright bird-dragons are juxtaposed since half of one upright creature and the entire intervening inverted one were omitted. From this point the repetition of the motif begins at the viewer's right and proceeds to the left; as on the Freer vessel, it repeats $8\frac{1}{4}$ times at 12.8 cm intervals. As above, the motifs run continuously around the vessel with no correlation between the motif joins and the mold marks. While measurements like those on the Freer vessel were not carried out, visual examination shows that the motif joins are closer together on the bottom band as are those on the Freer *chien*.

Mask Decor

The band of interlocked monster masks on the Freer vessel is 5.4 cm high. The major join (arrow 1, fig. 25) appears where part of the inverted mask is omitted and a discontinuity in the body bands is present. The first complete motif starts at the viewer's

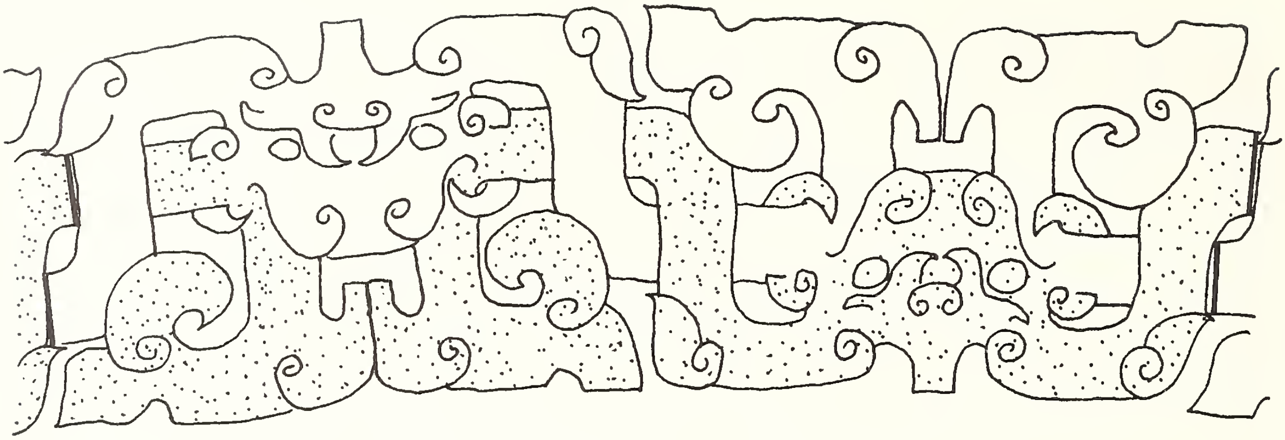

FIG. 26.—Mask motif from the *chien*, showing location of joins.

left, and the band proceeds to the right. The unit of repetition is a motif containing both one upright and one inverted mask, in that order (fig. 26). The joins are visible on the body bands where they cross, with the inverted mask on the viewer's left and the upright on his right. They are marked by thickened borders on the body bands and sometimes small extra ridges of metal. Like the bird-dragon decor, the mask decor runs continuously around the vessel across the mold marks. It is repeated eight times at intervals of 15.8 cm as measured from the left eye of one upright mask to the same point on the next upright mask.

This decor band is also 5.4 cm high on the Minneapolis *chien*. The major join occurs at the mold join (arrow 3, fig. 14) and resembles that on the Freer vessel. The unit of repetition and motif joins are like those on the Freer vessel as well. The motif is repeated eight times at 15.8 cm intervals and runs through the mold marks as stated above.

Handles

All the handles on both *chien* display identical decor and identical dimensions (5.6 cm from tip of horn to tip of horn; 2.5 cm between the pupils of the eyes). The V and M design appears 2½ times on each side of the handle and 4½ times on the undersides.

INSCRIPTIONS

Both vessels bear the same six-character inscription, which is located on the inside surface of each *chien* in slightly different positions. There is no evidence that any sort of mechanical device was used to produce them as the spacing of the characters differs, notably between the third and fourth characters which touch each other on the Minneapolis *chien* but do not on the Freer piece (figs. 4 and 5).

Gettens believed that the inscription on the Freer vessel is incised and adds that such inscriptions are common in the late Chou period. He notes that the lines are sharp, chatter marks and doubled grooves from repeated tool strokes are visible, and that the lines taper as one would expect from an incising technique.[36]

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[36] Pope, *et al.*, *The Freer Chinese Bronzes*, vol. 1, p. 482.

The edges of the characters on the Minneapolis *chien* are also sharp, and the lines become both deeper and wider in the middle of the stroke. There is faint evidence that the inscription may have been etched, however; the lines appear slightly undercut, their inside contours are slightly granular in texture (though later corrosion could be responsible), and the corners of the strokes are faintly rounded on the inside. The suggestion that the lines are etched is most tentative, however; the whole question as to whether ancient inscriptions were ever etched is an open one, since we do not know if acids strong enough to etch bronze were in use at the time. Wan Chia-pao believes that such acids were unknown in ancient China and that inscriptions were generally cast in, at least in the Shang period.[37]

SUMMARY AND FURTHER PROBLEMS

Some conclusions about the fabrication of the pair of *chien* can be drawn. The most striking feature in this pair of vessels is that their decor is completely modular—i.e., six basic decor motifs are repeated to produce the total design.

Superimposition of transparencies of the masks indicates that each mask motif is identical in every detail both within a single vessel and between the two vessels, indicating that these designs were all produced from the same master pattern block. Careful comparison of photographs and the measurements given above indicate that all bird-dragon motifs are also identical within each band, between both bands, and on both vessels; thus, all of these units must also have been produced from the same master pattern block. However, the question of how the concave top band and the convex bottom band were reproduced from the same master pattern block remains to be answered.

Since basic units of length were used in replicating the cowrie and braid motifs, it appears that these lengths were employed where convenient and arbitrarily shortened when required. Probably the same master pattern blocks were used to produce these motifs on both vessels and the slight irregularities result from the difficulties of accurately laying such long segments of decor. The decor motifs on the rims of the vessels are also virtually identical in both *chien.*

The eight handles and four rings on the vessels also appear to be identical. If they were produced from a single pattern, the question arises as to how one can account for the absence of seams on the handles. It is also interesting to note that the handles are soldered over bosses on the vessels rather than cast on.

While the pair of *chien* exhibit "sectionalism of decor" to an extraordinary degree, they do not exhibit sectionalism of the pattern/mold at all, as the motifs repeat continouously around the circumferences of the vessels regardless of the vertical divisions of the molds. In addition, since the register of decor motifs from one band to the others differs on the two vessels and variations occur in repetition of the braid and cowrie motifs, it is evident that the vessels were made from not one but two complete patterns and/or four-piece mold assemblies of virtually the same dimensions. In both cases numerous chaplets or spacers were used to maintain a uniform distance between the core and the mold proper, but precisely how the two patterns and/or mold assemblies were produced is a question still to be answered.

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[37] Wan Chia-pao, private communication.

It is also necessary to determine whether a positive master pattern block was used as a loose piece to produce a negative impression directly in the mold or whether a negative impression made from a positive master pattern block was used to produce positive decor on the complete pattern; the mold would then be slip-cast or impressed from this complete pattern. Another question which arises is whether the master pattern blocks were curved to fit the arcs of the vessel or whether they themselves were flat and only the impressions in clay taken from them were curved for incorporation into the mold or pattern.

To summarize, it is clear that two similar patterns and/or mold assemblies were prepared by replicating the decor motifs on the two *chien* exactly, using a mechanical means. To answer the additional questions raised above, data from the Hou-ma foundry and further observations on the pair of *chien* must be considered.

THE FABRICATION OF THE PAIR OF *CHIEN*

The remains of bronze foundries at Hou-ma, in Southern Shansi, are as valuable a source of information about late Chou bronze casting as the An-yang find was for that of the Shang period (fig. 3). This site was excavated in 1959 and yields the only late Chou foundries studied thus far. On the basis of stratification and the designs on the molds, Chang Han, one of the principal excavators, dates the find from the middle Ch'un-ch'iu to the middle Chan-kuo period.[38] More precisely, the foundries were probably in use from the establishment of the Chin capital at Hsin-cheng in 584 B.C.[39] to the fall of the Chih family in 453 B.C.

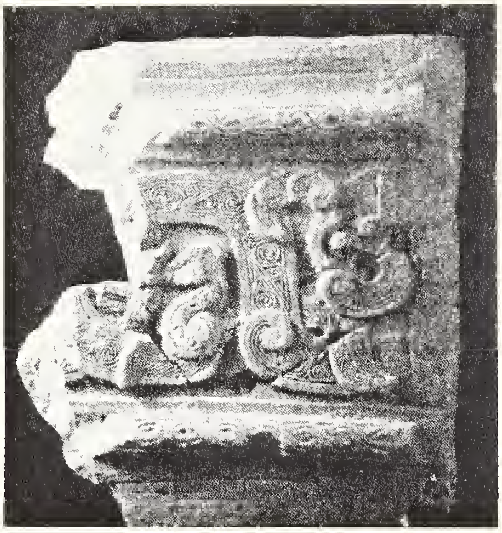

FIG. 27.– Fragment from Hou-ma (after *Wen-wu*, no. 10 (1961). Figure 4).

It is quite probable that the Freer and Minneapolis *chien* were fabricated at Hou-ma, for the foundries there were located near the Chin capital at the time the *chien* were made. In addition, the inscriptions of the *chien* indicate that they were commissioned by the Chih family who undoubtedly resided in Hsin-cheng. One of the fragments from Hou-ma offers a further connection between that site and the Freer and Minneapolis vessels as it bears a bird-dragon differing from those on the *chien* only in the filling lines on the body band, which is a hook-and-volute design on the fragment and a running spiral on the *chien* (fig. 27).

Chang Wan-chung's 1962 study of the Hou-ma fragments[40] is analogous to Karlbeck's study of the An-yang molds, as both are preliminary attempts to reconstruct casting techniques by examining the archaeological remains of the most important known foundry sites of their respective periods. It is important to note that Chang Wan-chung's work pre-dates that of Gettens, Fairbank, and Smith, while Barnard's work was almost certainly not available to him. Therefore it is not surprising that his findings underscore the continuity of Chinese foundry practice between the Shang and late Chou periods rather than the differences between them, as his account stresses such aspects of casting as assembling the molds and arranging the gating rather than the issues of sectionalism or decor replication.

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[38] Chang Han, "*Hou-ma Tung-Chou*," p.1.

[39] Max Loehr, *Ritual Vessels of Bronze Age China* (New York: Asia Society, Inc., 1968), p. 143.

[40] Chang Wan-chung, "*Hou-ma Tung-Chou*."

However, some of Chang Wan-chung's observations on the Hou-ma material are indirectly pertinent to the issue of sectionalism. First, the fine mold material he describes,[41] unlike the coarser An-yang fabric, is capable of transferring subtle modeling repeatedly without loss of detail, and thus makes possible the use of master pattern blocks to replicate decor motifs.[42] Chang also alludes to the idea, which Barnard further developed,[43] that many identical patterns for appendages were slip-cast in molds taken from master patterns at Hou-ma: Chang cites a pattern for the leg of a *ting* which has a seam running through the design which must have been a mold join.[44]

As for the use of master pattern blocks, and the issue of whether decor motifs were placed on the patterns or directly in the molds, Chang is vague. He first states that the mold fragments for ritual vessels found at Hou-ma fall into three categories: "mother molds" (patterns and/or master pattern blocks); "outer molds" (the mold proper); and "inner molds" (cores).[45] He further states that the "outer molds" were reproduced from the "mother molds"[46] but does not elaborate. It is probable that Chang was thinking in terms of impressing molds from complete, fully-decorated patterns. Barnard, on the other hand, is certain that some of the Hou-ma fragments carved in low relief are indeed master pattern blocks which were used to replicate decor motifs in the negative for direct incorporation in the mold.[47] It is difficult to tell from the published photographs whether all such fragments are parts of fully-decorated patterns or whether they are master pattern blocks bearing one motif only; perhaps both types of fragments are present. Yet at least some of the Hou-ma fragments must be master pattern blocks, especially those with flanges (fig. 7).

To summarize, the material evidence from Hou-ma, where the Freer and Minneapolis *chien* may have been fabricated, provides further information on how both appendages and decor motifs were replicated.

Thus the vessels' rings and handles were undoubtedly cast from individual molds made from master patterns. The rings may have been cast in open molds, and the striations on the reverse produced in finishing

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[41] *Ibid.*, p. 5 of translation (see footnote 23).

[42] The present writer has seen some of the patterns and molds from Hou-ma at the Royal Ontario Museum, Toronto. The fabric of these objects is indeed white and fine. None of the fragments thought to be master pattern blocks was seen.

[43] Barnard, *Metallurgical Remains*, pp. 57–58.

[44] Chang Wan-chung, "*Hou-ma Tung-Chou*," pp. 6–7.

[45] *Ibid.*, pp. 3–4. Barnard comments on the need to clarify Chang's confusing terminology. (*Metallurgical Remains of Ancient China*, p. 57.)

[46] *Ibid.*, pp. 8–9.

[47] Barnard, *Metallurgical Remains*, p. 58.

(arrow 2, fig. 25). While all of the four rings display identical decor, one of the rings of the Freer *chien* has a peculiar bulge (arrow 2, fig. 11); this difference in shape indicates that the four rings were not cast from a single, reuseable mold.

The fabrication technique of the eight identical handles is more complex. They too must have been cast in molds taken from a single pattern. However, the way the molds were taken from the original is difficult to ascertain as the complex ears and horns of the heads create shapes that would be hard to draw without damaging the mold. Possibly molds were taken in sections and retouched with slip from the back before they were fired and the cores inserted. This procedure could have been carried out since the handles are somewhat open at the back. No chaplets would be needed as the handles are open at the ends and the core could thus be secured at both ends. However, a chaplet-like element does appear on the bottom of one of the handles of the Minneapolis *chien.* (arrow 2, fig. 17).

Differences in the register of motifs in the various decor bands on the Freer and Minneapolis *chien* clearly show that two complete molds and/or patterns were used to produce the pair of vessels. Two other factors are virtually certain. First, since all the decor bands run through the mold marks, the motifs were placed all the way around the circumferences of the vessel before the vertical mold divisions were made. Second, flat master pattern blocks were probably used to impress the motifs on strips of clay which in turn were set into the molds or patterns, as identical master pattern blocks were employed to produce the upper and lower bird-dragon decor bands which have opposite curvatures. However, an unresolved issue in the fabrication of the pair of *chien* is whether master pattern blocks bearing the designs in the positive were used to replicate motifs in the negative for direct incorporation in the mold, hence eliminating the need for a pattern, or whether negative impressions from the master pattern blocks were used to produce decor in the positive on the patterns.

Attempting to answer this question on the basis of visual evidence alone is difficult; study of radiographs yields little further information. Direct study of the Hou-ma fragments would undoubtedly be helpful. But it is possible to describe the alternatives and determine which is more likely in terms of existing data.

The idea of placing the decor motifs in the positive on the complete pattern for the vessel cannot be absolutely dismissed. This possibility involves preparing two smooth, blank patterns, perhaps by casting them in a mold (fig. 28).[48] This method would yield two patterns of identical dimensions required for the two *chien.* Positive master pattern blocks for the decor motifs to be replicated would be used to prepare blocks in the negative (figs. 29 and 30), which in turn would be impressed on small slabs of clay (fig. 31). These slabs would be placed on the pattern, starting at an arbitrary point and cut off when the circuit of the vessel was complete (fig. 32). The convex and concave decor bands could then be bent to the appropriate curvature in the process of application. A separate pattern might be required for the rim of the vessels and its

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[48] Chang Wan-chung mentions preparing cores in smooth, negative "mother molds." (Chang Wan-chung, "*Hou-ma Tung-Chou,*" pp.10–11). The basic shapes for patterns could have been prepared in a similar way.

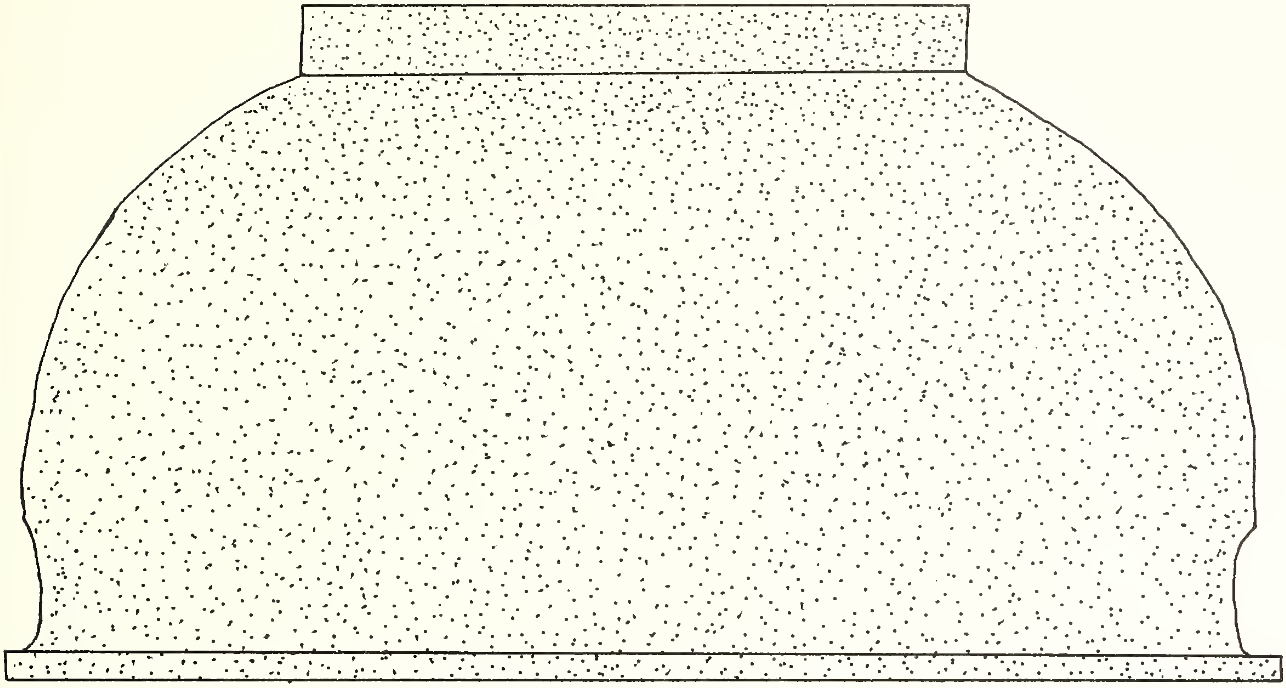

Fig. 28.—Blank pattern.

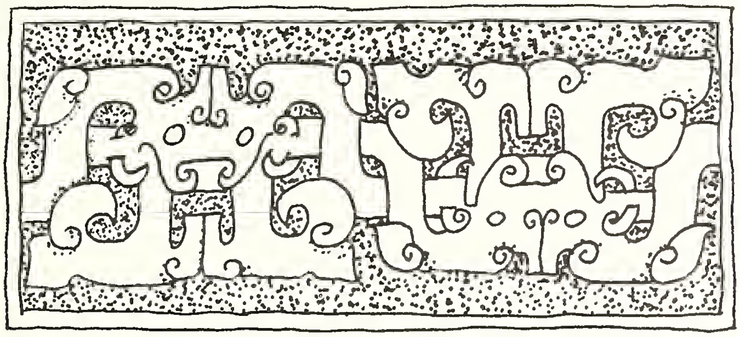

Fig. 29.—Master pattern block with design in positive relief.

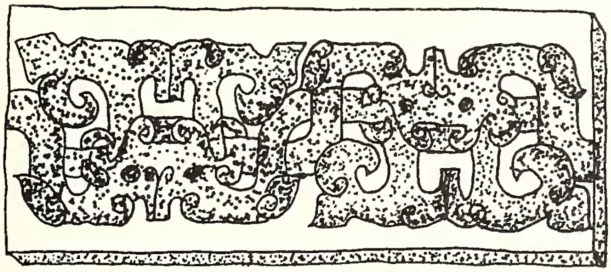

Fig. 30.—Block with design in negative relief.

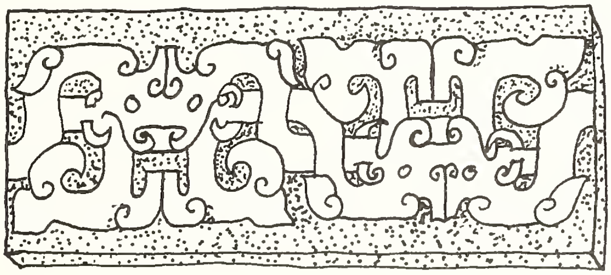

Fig. 31.—Slab of clay with design in positive relief.

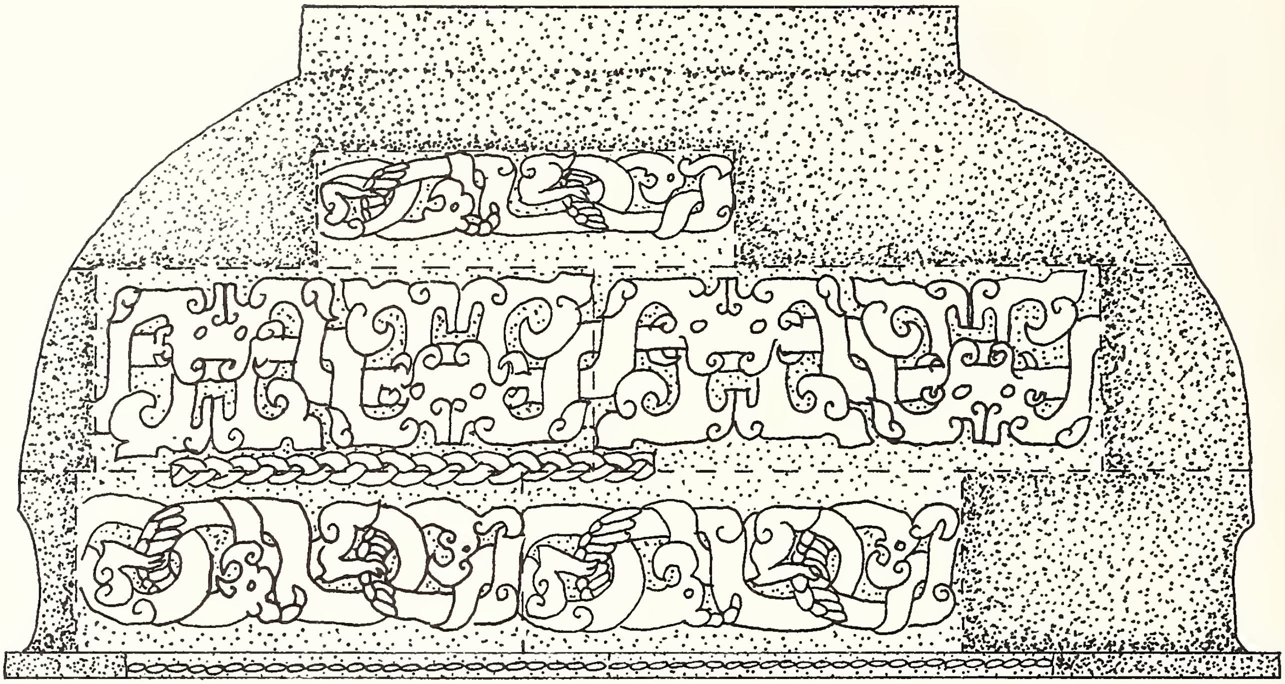

Fig. 32.—Slabs of clay applied to the pattern.

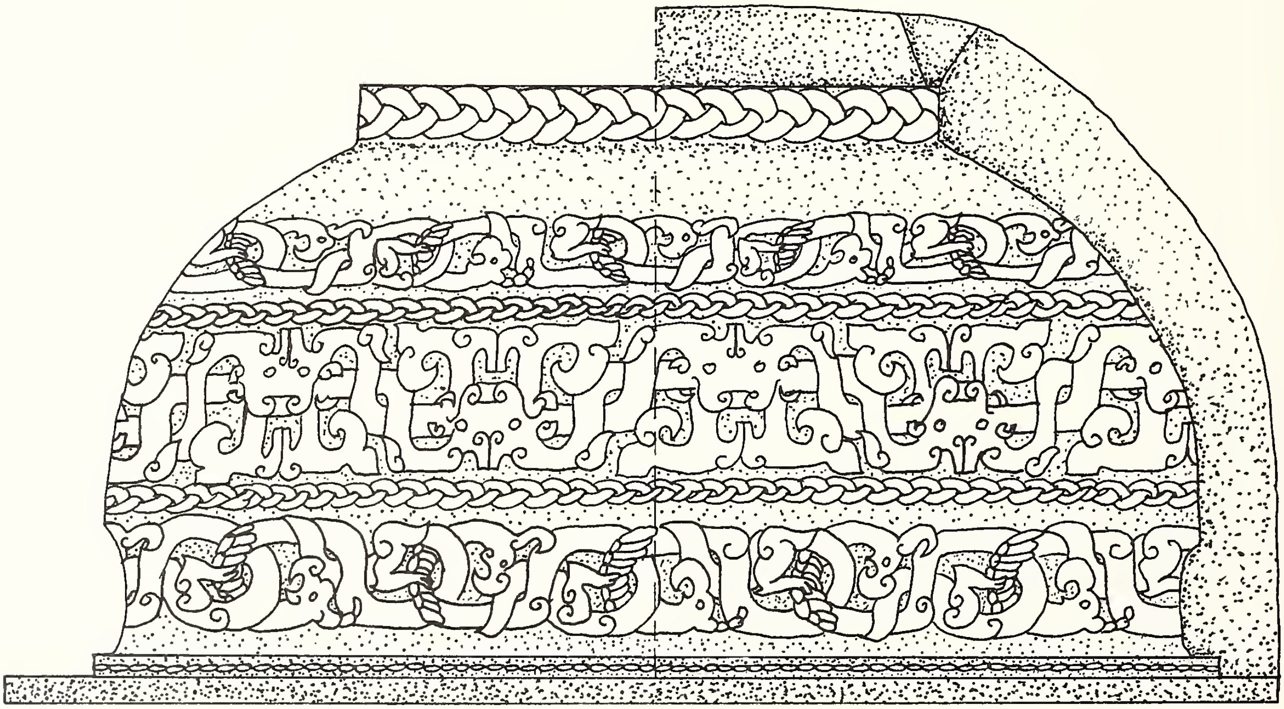

Fig. 33.—Formation of four-piece mold from the pattern.

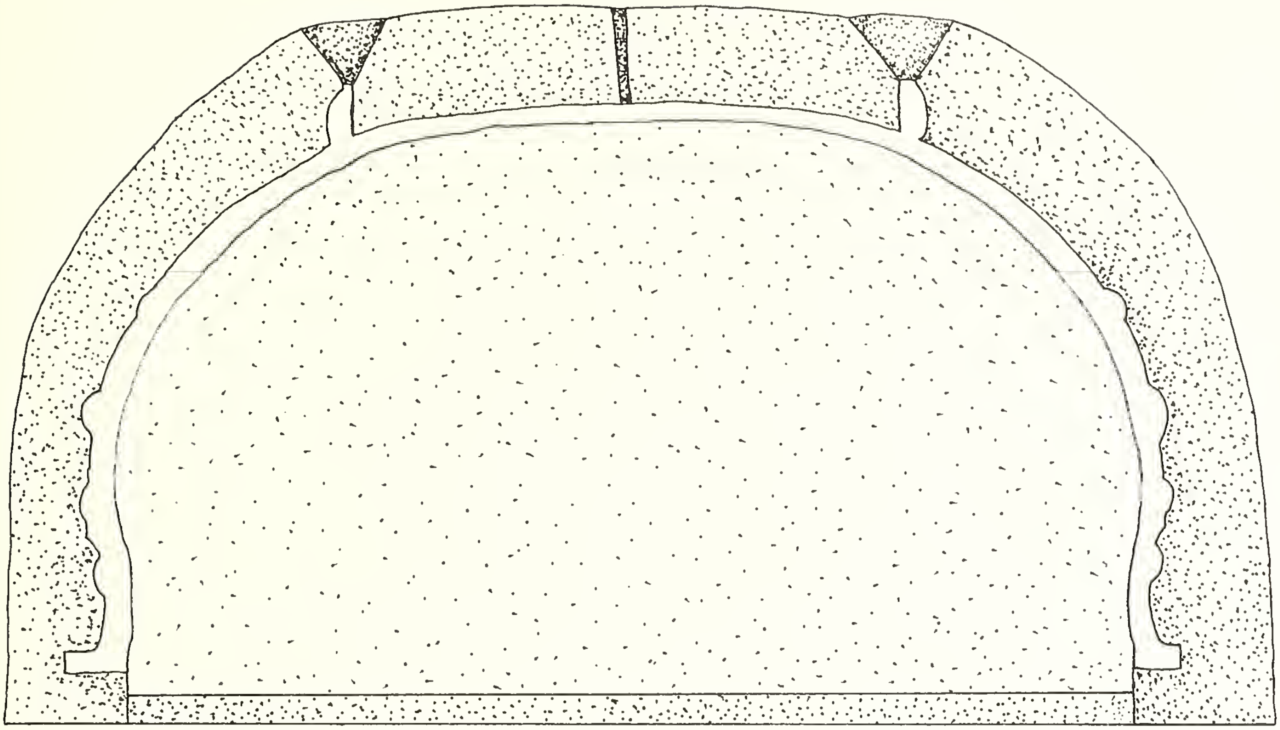

FIG. 34.—Complete mold assembly with core.

decor. Sections of braid could be made in molds and applied to conceal the horizontal joins between registers of decor.[49] The patterns would be dried slowly, fired, and the molds produced from them by impressing plastic clay on them, letting it dry slightly, and quartering it for removal (fig. 33). A core could be made by impressing clay in the finished mold and trimming it down or by impressing it in a specially prepared blank mold (fig. 34). Since cores found at Hou-ma were of different composition than the patterns,[50] it is evident that patterns were not trimmed to form the cores.

The above scheme would involve several transfers of the designs, but the very fine, porcelain-like ceramic material found at Hou-ma may well have been capable of retaining the detail transferred at each step. Furthermore, Barnard's idea of first-and-second generation molds for casting appendages involves the same number of transfers.

The procedure outlined above also accounts for several peculiarities on the vessels themselves. First, several areas on the Freer *chien* have very shallow triangle-and-volute patterns as if insufficient pressure was exerted on the negative block to impress the decor fully on the clay. One such area appears on the middle decor register on the Freer vessel (arrow 4, fig. 15), while in a similar area in the same location on the upper register, the triangle-and-volute design has been incised by hand (arrow 5, fig. 15). In addition, while

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[49] It is interesting to note that master pattern blocks from Hou-ma bear rope and braid elements as well as the figurative decor motifs. On the other hand, the braid units on the pair of *chien* repeat at intervals unrelated to the joins in the figurative motifs.

[50] Chang Wan-chung, "*Hou-ma Tung-Chou*," pp.3–4.

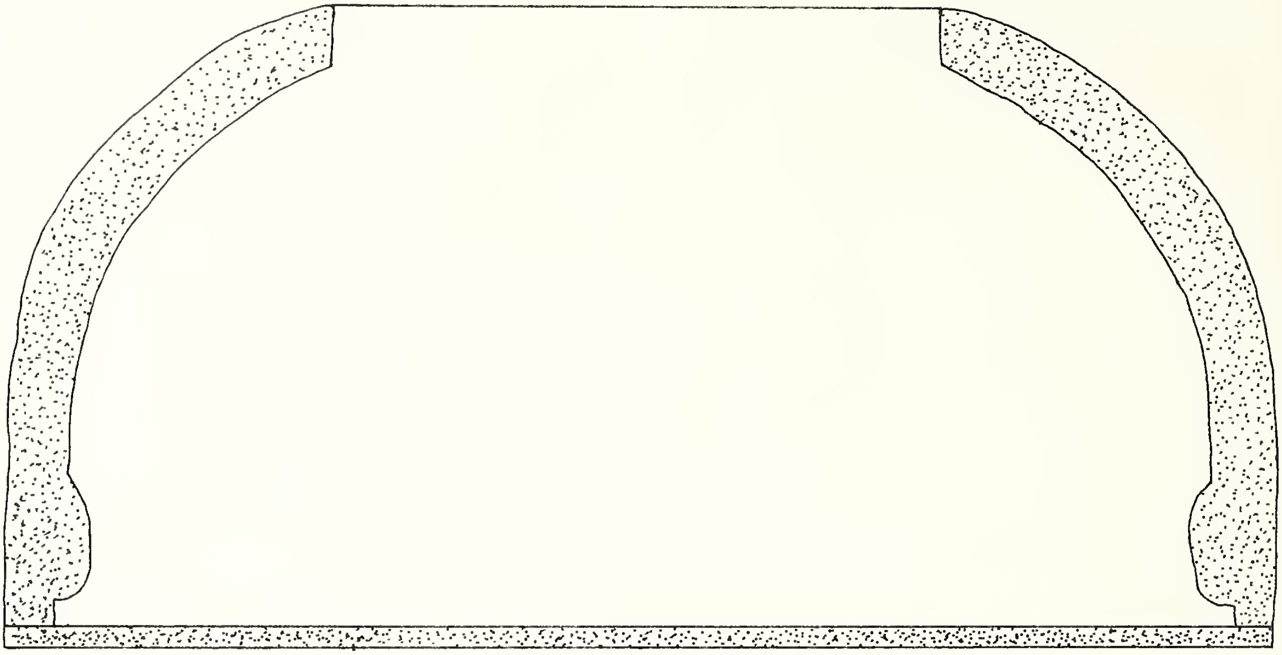

Fig. 35.—Template for mold cavity.

some of the joins in the braid motif are sharp vertical lines as would be made by direct stamping in a mold surface, others are in the form of indentations, as if the ends of appliqué sections had been pressed rather than stamped into place (arrow 3, fig. 17). Also, the edges of the braid in many areas appear to have been smoothed by hand.

The idea of decorating the mold surface directly resembles that based on modern Japanese foundry practice as proposed by C.S. Smith and, more recently, Noel Barnard. If this scheme applies to the pair of *chien*, the following procedures could have been employed. It is very likely that the mold surface to be decorated was supported on a sweep-molded template of the desired size and shape (fig. 35). Also, the template could be divided horizontally to facilitate working inside the cavity, as seen in the Enjo Foundry (fig. 36); and the vertical divisions could be pre-planned as well to facilitate removal of the inner mold surface.

The decor bands would be prepared by impressing slabs of clay on the flat master pattern blocks[51] (figs. 37 and 38) and inserting the slabs in each horizontal mold section (fig. 39). As Smith mentions, this technique could easily produce both concave and convex decor registers made from the same flat master pattern block, as seen in the pair of *chien*.[52] This scheme would also account for the motifs' beginning at an arbitrary point and continuing uninterruptedly until the circle is completed. It is even possible that vessel designers deliberately staggered the end points of each decor register to render the major joins less

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[51] A parting agent, of course, is necessary. At the Enjo Foundry lamp black is used.

[52] Smith, "Metallurgical Footnotes," p. 113.

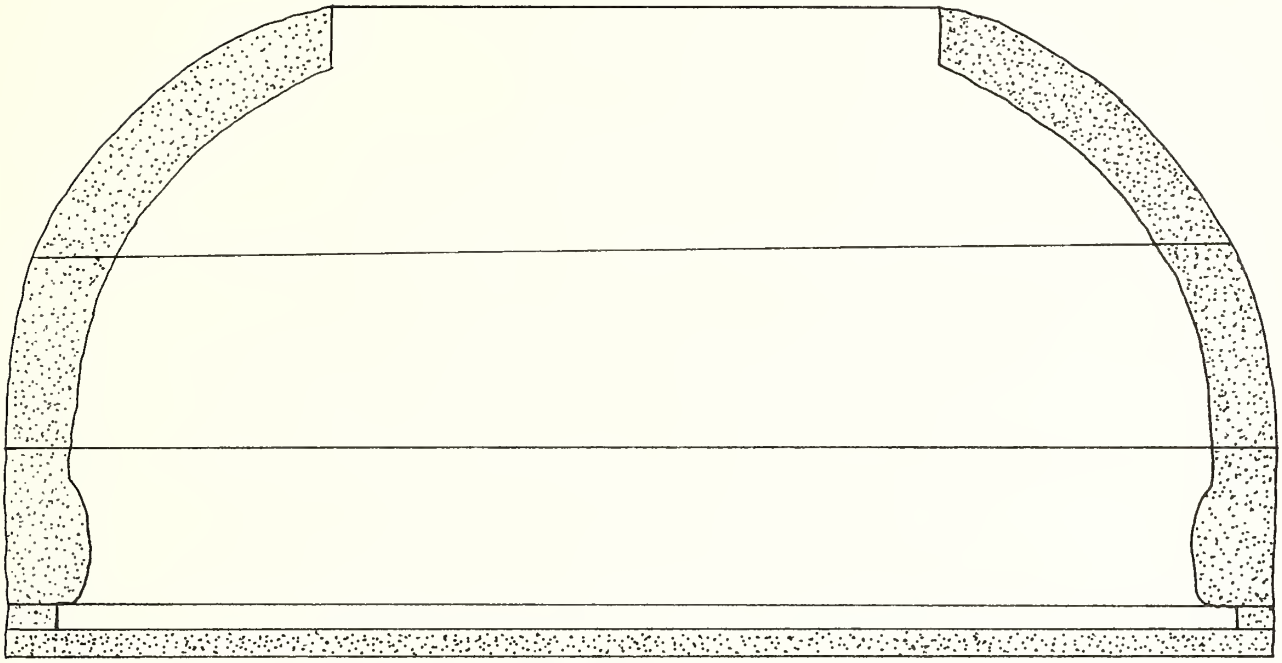

FIG. 36.—Template divided into horizontal sections.

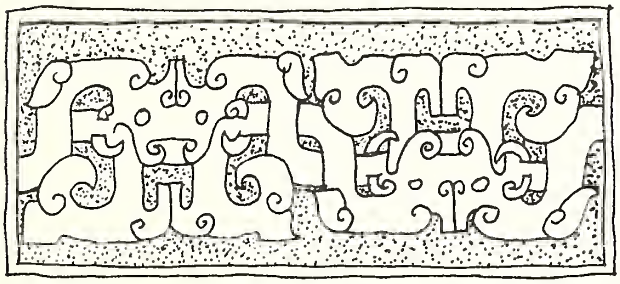

FIG. 37.—Master pattern block design in positive relief.

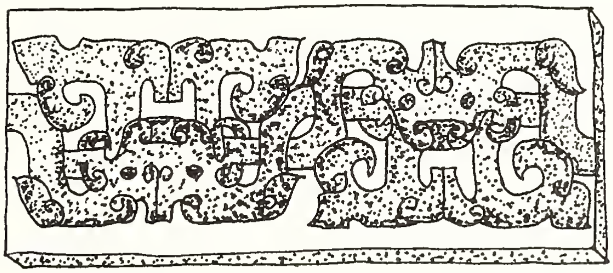

FIG. 38.—Slab of clay with design in negative relief.

noticeable and thus emphasize the horizontal continuity of this decor style.

When this operation was finished, the horizontal sections could be assembled. The idea of horizontal mold sections is supported by the observation that the braid lies at the center of a clear band which is in relief and butts up against the decor motifs in both registers. This clear band in relief could have been produced by placing the assembled horizontal mold sections on a wheel and trimming the areas between the decor registers with a knife; in fact, at some points the clear area merges into the decor band (arrow 4, fig. 14).[53] The braid would then be stamped directly into the assembled mold with loose pieces.

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[53] The whole idea of the braid and/or clear band separating the decor registers as a device used to conceal the joins between the blocks used to form the mold is an important one, and it pervades the whole Li-yü or Hou-ma style of vessel production.

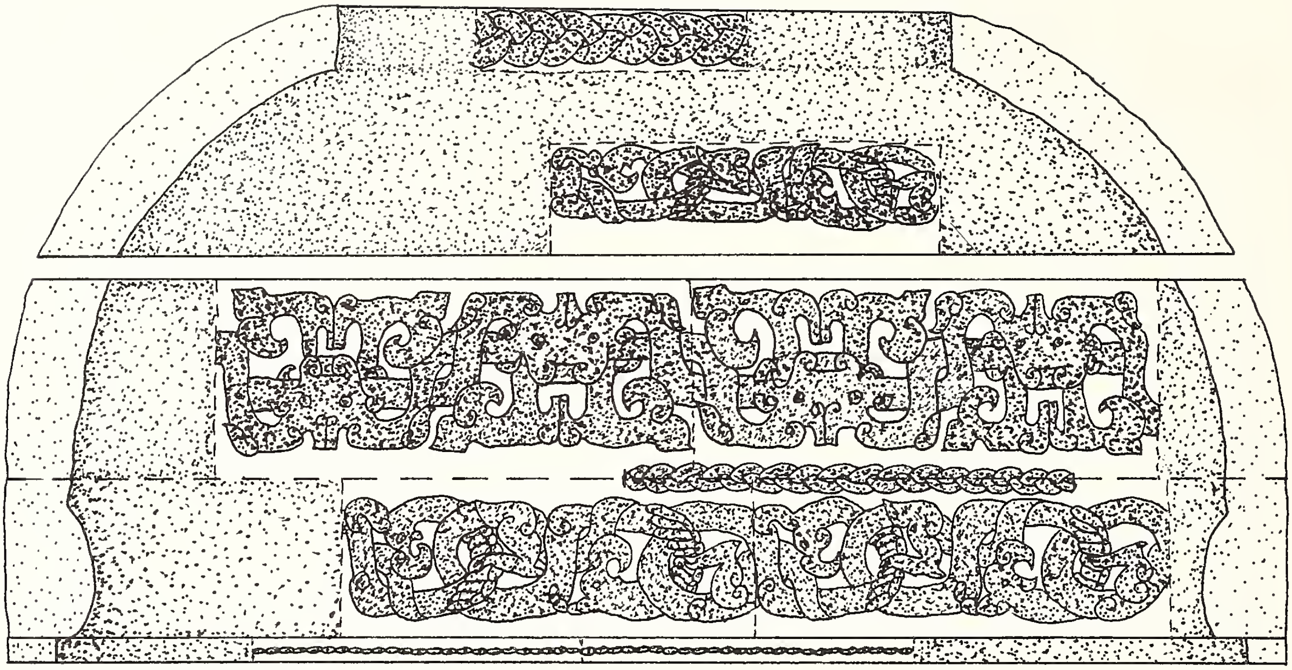

Fig. 39.—Slabs of clay applied to sections of the template.

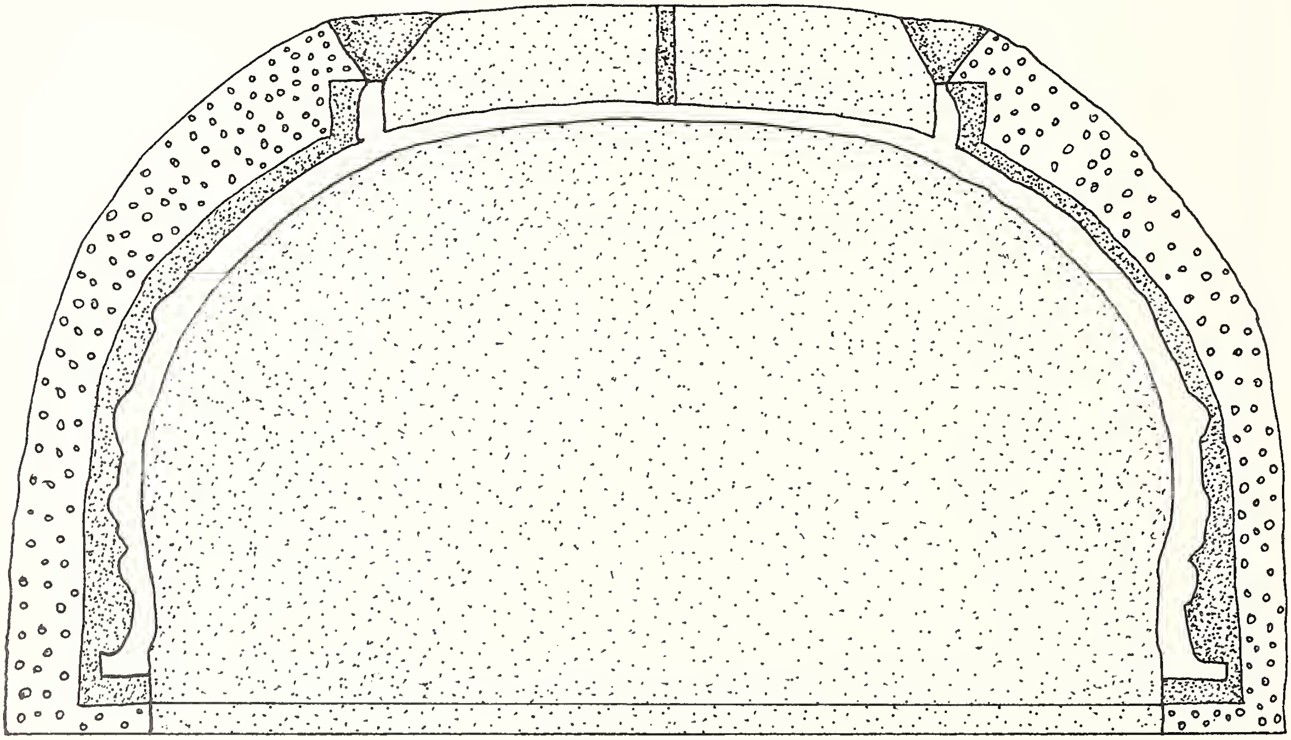

Fig. 40.—Complete mold assembly with core.

When the mold was leather-hard, it could be quartered along the pre-planned vertical divisions and the outer surfaces reinforced with coarser ceramic material, dried, and fired as described by Chang Wan-chung.[54] Cores for the principal cavity and foot could be formed in blank molds of appropriate size and shape, or in the fired mold for the vessel with subsequent filing of the dry core to produce the casting space (fig. 40). While the cores were probably prepared with damp clay and then dried, the question of whether they were fired should be left open. In the Enjo foundry, they are not fired. Firing should produce shrinkage, while filing down of the dried core to produce casting space would leave a core which would not change shape subsequently. Cracking of the cores is often evident, especially in the unfinished feet of vessels; in fact, this cracking is usually in the direction of shrinkage (rather than expansion) showing that a partial firing might be taking place during casting. Cores are often fired enough to be datable by thermoluminescence, but this may be firing by contact with the molten bronze.[55]

In the reassembly of the core and mold sections, chaplets and gates could be added. After the final mold assembly and addition of the gating, the whole assembly could be heated and the metal poured. The handles and rings could be molded and cast separately as described; they would be brazed onto bosses on the vessels, probably with a high-tin alloy. Finally, after post-cast finishing, the inscriptions could be incised.

Applying decor to the mold surface is the probable method used to produce the pair of *chien*.[56] Visually, the products of either method would undoubtedly be very similar. However, there are two strong arguments in favor of this second scheme. First, it requires only two transfers of decor—that from the master pattern block to the mold surface, and from the mold to the finished casting. Second, this scheme eliminates the question of why the founders would prepare two similar patterns when both sets of molds could have been impressed from a single pattern.

No single pattern ever existed. The bronze caster did not start with a pattern (or model) of the finished bronze, but rather began with the molds. The master pattern blocks were used to repeat six motifs on the mold; "sectionalism" occurs not in the mold itself, but in the decor replication techniques employed.

Thus, on the balance, the data from the Freer and Minneapolis *chien*, combined with that from Hou-ma, support the theory that the predominant method for casting late Chou vessels in the interlaced zoomorph style was to use master pattern blocks to produce slabs of clay with decor in the negative incorporated directly in the mold surface.

ACKNOWLEDGMENT

The author would like to thank W. T. Chase of the Freer Gallery for providing

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[54] Chang Wan-chung, "*Hou-ma Tung-Chou*," pp. 8–9.

[55] W. T. Chase, private communication.

[56] When the Freer and Minneapolis *chien* were first closely studied in 1971 and 1973, the present writer favored the method of placing decor blocks on the model. On re-examination of the vessels and other evidence in 1977, the arguments for direct decoration of the mold surface appear much stronger.

radiographs and detail photographs of the vessels, access to Freer Gallery of Art records, translation of Hou-ma literature, and other invaluable aid. All photographs and radiographs, except Figure 5, are courtesy Freer Gallery of Art.

She would also like to thank Dr. Jui-Hsi Chou, formerly of Oberlin College, for his valuable criticism.

GLOSSARY

Decor: The design seen on the surface of the bronze.

Motif: A unit of design, here used with the particular connotation of one segment of decor which would be repeated to make a register of the vessel decoration. For instance, Figure 20 shows the motif of two interlaced dragons; motif joins are seen in the middle of the bodies of the upward-facing dragons; one full motif unit and sections of two others are seen here.

Pattern: A full-size positive representation of the object to be cast (or some portion of it).

Loose piece: A small pattern, often in the form of a stamp, impressed directly in the mold.

Master pattern block: A full-size positive representation of a motif. Impressions taken from the master pattern block are used to repeat a motif as described above.

TECHNIQUES OF SILVERSMITHING IN THE HORMIZD II PLATE

BY DONALD F. GIBBONS*
KATHARINE C. RUHL*
AND DOROTHY G. SHEPHERD**

The collection of Sasanian silver objects in the Cleveland Museum of Art includes a silver plate depicting the king Hormizd II hunting lions (fig. 1). A full description of the plate together with a discussion of its iconography and stylistic characteristics has been published.[1] The plate is linked to a group of other plates similar in subject matter, style and also in technical aspects. A treatment of the technical problems of this and other Sasanian silver objects[2] included some of the data presented in this paper. Further studies of the Hormizd II plate and some related pieces have been completed at Case Western Reserve University and the Cleveland Museum of Art. A re-evaluation of all the data now allows a clearer picture of Sasanian silversmithing techniques to emerge.

The Hormizd II plate is typical of a large number of Sasanian silver plates with relief design in that the low relief is part of the plate itself, while the high relief elements of the design are shaped separately and inserted into the top surface of the plate.

The plate was studied by visual examination under a low power microscope and by radiography. Metallography was performed on two specimens (figs. 2, 3) and chemical analysis of one of the specimens was obtained by electron beam microprobe and X-ray fluorescence analysis.

The larger of these specimens was the only remaining fragment of the horse's proper right foreleg which is part of the low relief of the plate. After examination of one edge, (A, fig. 3), the fragment was replaced in the plate. This specimen (fig. 6) includes the entire cross section of the leg, but does not include any part of the background.

The section shows first that the plate is made of silver sheet, hammered out from the ingot with a reduction of about eight to one. The low relief of the leg was made by removing metal from the top surface of the plate to form the outline and three-dimensional contours of the limb.[3] Silver was undoubtedly also removed from the surrounding background, especially near the edges of the relief, as radiography shows slightly thinner metal

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[1] D. G. Shepherd, "Sasanian Art in Cleveland," *Bulletin of the Cleveland Museum of Art*, vol. 51, no. 4 (April 1964), pp. 66–95.

[2] D. G. Shepherd, "Some Problems of Sasanian Silver," *Fifth International Congress of Iranian Art and Archaeology*, Special Publication of the Ministry of Culture and Arts, Tehran, Iran (1972), vol. 1, pp. 326–352.

[3] In this discussion, we are not attempting to identify the special tools or operations used in forming the relief. We do wish to make clear the difference between metal *removal* and metal *movement*. The former is characterized by carving, chiseling, grinding, scraping, and engraving; operations in which a portion of the silver is cut away from the main body of the metal. Metal movement is illustrated by hammering, sinking, raising, repoussé, crimping, chasing, tracing, punching, and burnishing, and involves silver which remains part of the body of metal, but is displaced. We have used several of the above terms in our discussion but, in general, we do not insist on the specific operation named, simply the category to which it belongs.

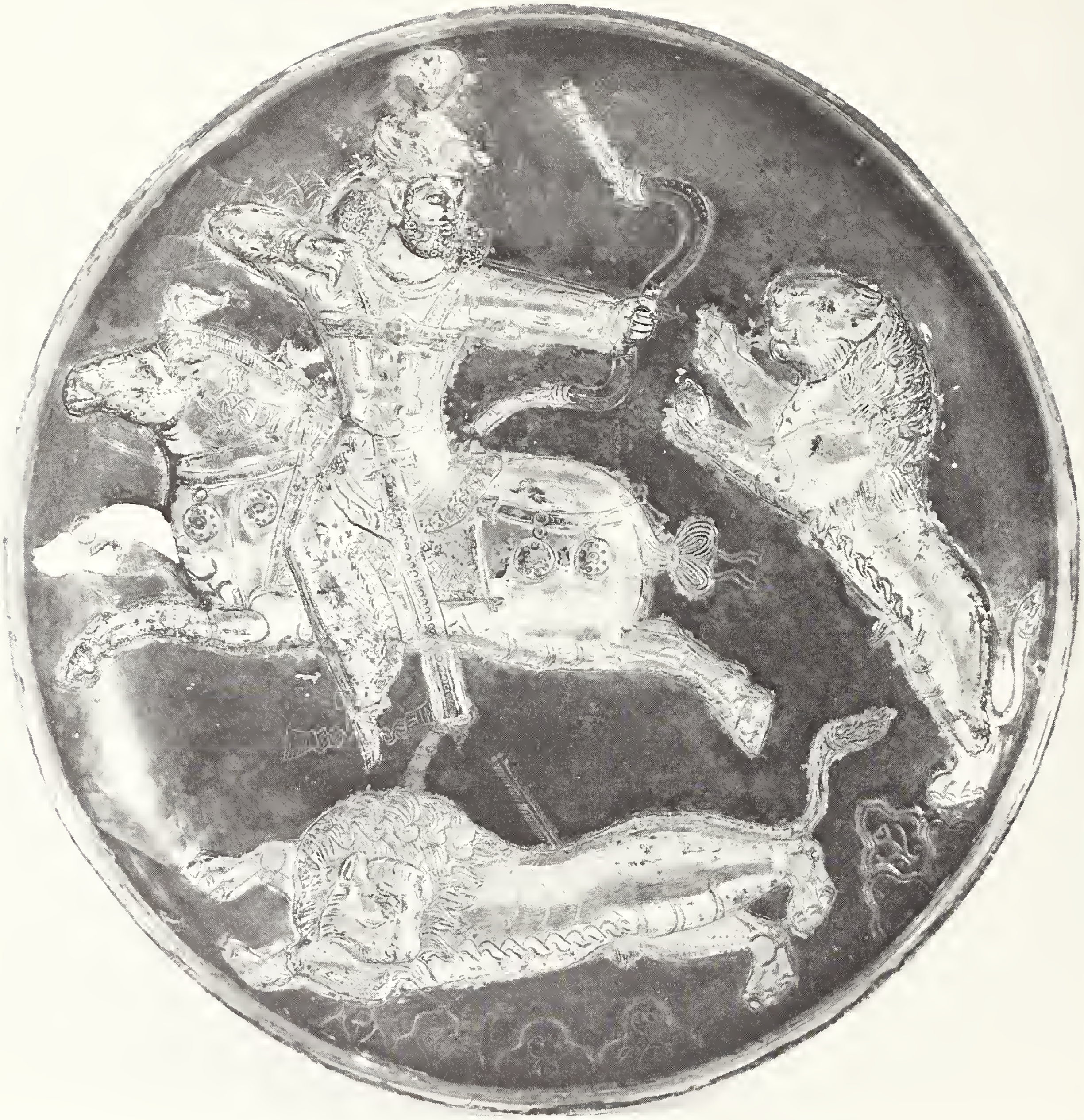

Fig. 1.—Hormizd II plate, front. The Cleveland Museum of Art, Purchase from the John L. Severance Fund. (62.150).

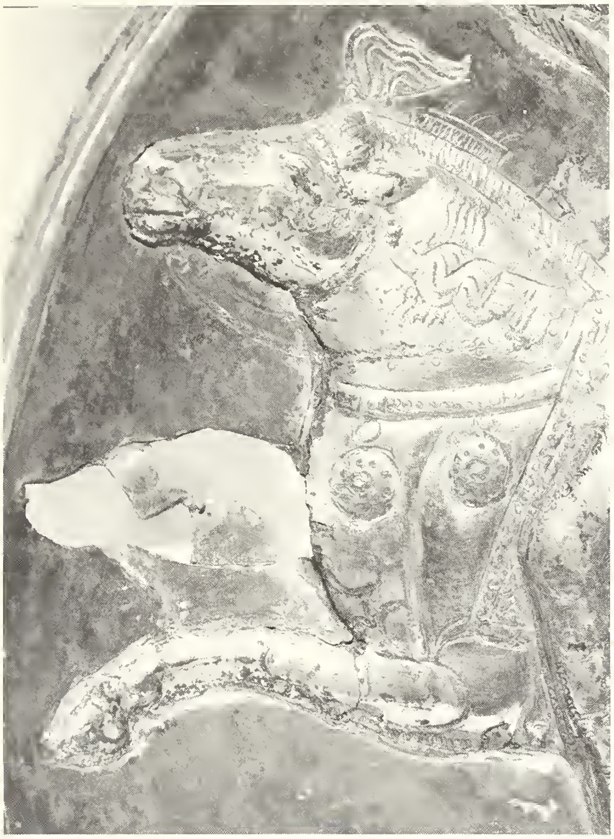

FIG. 2.—Detail of the Hormizd II plate: the area of the chest and forelegs of the horse.

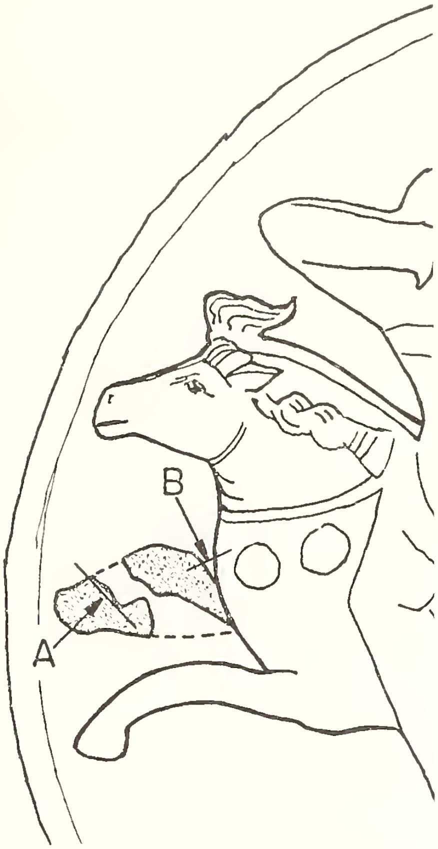

FIG. 3.—Diagram showing the locations from which specimens were obtained.

in the background than in the relief portions (fig. 4). The difference in thickness is, however, actually less than it appears to the eye, attesting to the craftman's skill in achieving his desired effect. Measurements from the plate give the average thickness of the plate at the background to be 0.64 mm compared with 1.0 mm on the low relief. A cross section through a relief element and the nearby background would appear as in Figure 5a, rather than Figure 5b. That this shaping and modeling was done by removing metal from the top surface, rather than by repoussé, followed by evening off the bottom surface, is demonstrated by the flow lines in the silver; they run parallel to the bottom of the plate, but are intersected by the contours of the top of the plate.[4] Repoussé would have resulted in an appearance in the flow lines as in Figure 5c. Instead, the observed structure is shown in Figure 5d. Metallographs (figs. 7–12) show details of the microstructure. In Figure 8, three strokes of the chisel

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[4] The etched metallographic sections show the flow pattern of the metal caused by cold working. Initially, after casting, the alloy consists of equiaxed grains of the silver-copper solid solution as well as a small amount of copper-rich eutectic between some of the grains. The cold working elongates the grains and eutectic in a direction perpendicular to the force applied by hammering. On etching, the copper-rich eutectic is attacked preferentially and thus the elongated grains show the flow pattern illustrated. The gilding on the surface is not attacked by the etch and therefore appears as a smooth featureless layer, except for its spongy nature.

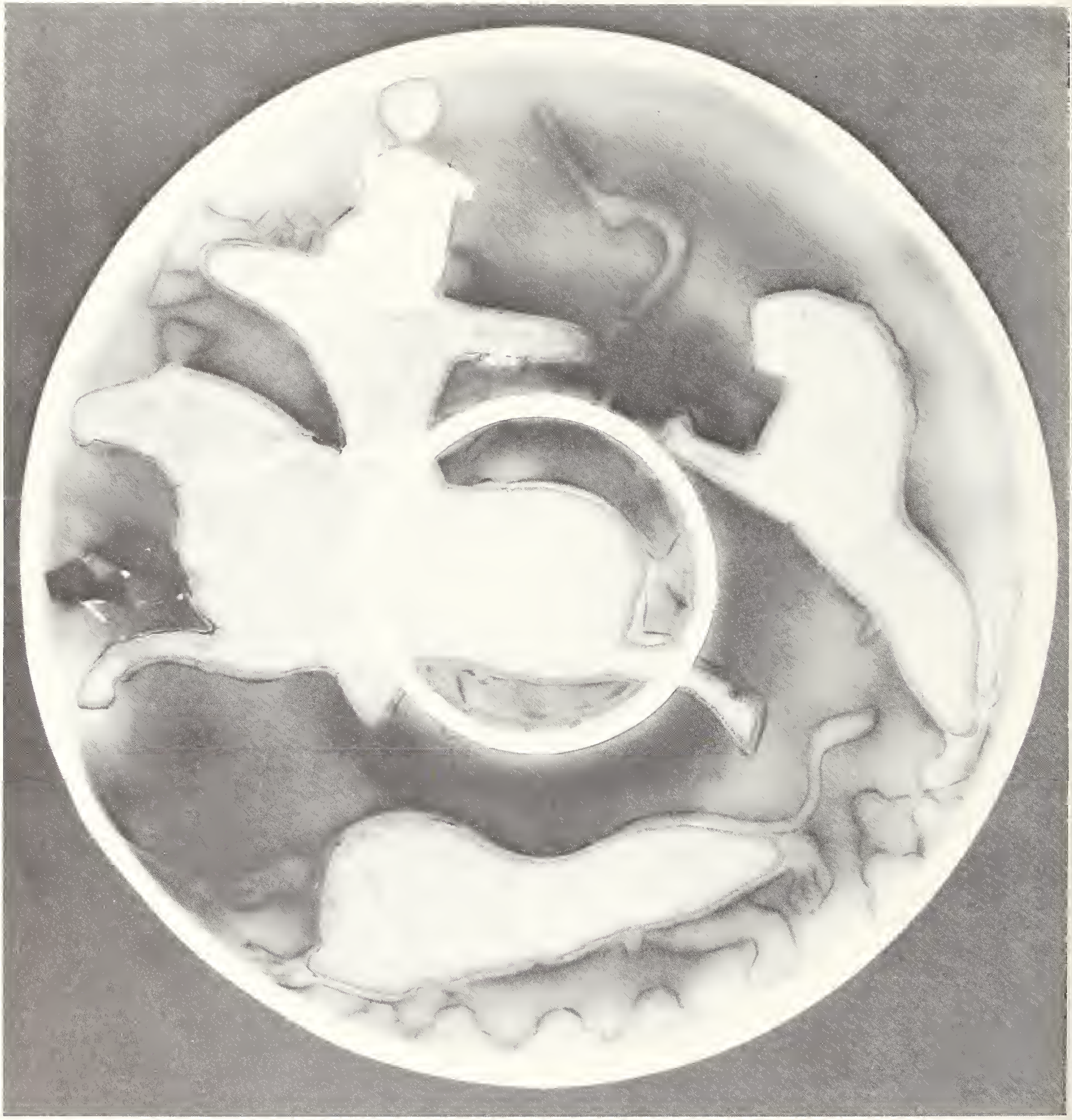


FIG. 4.— Radiograph of the Hormizd II plate.

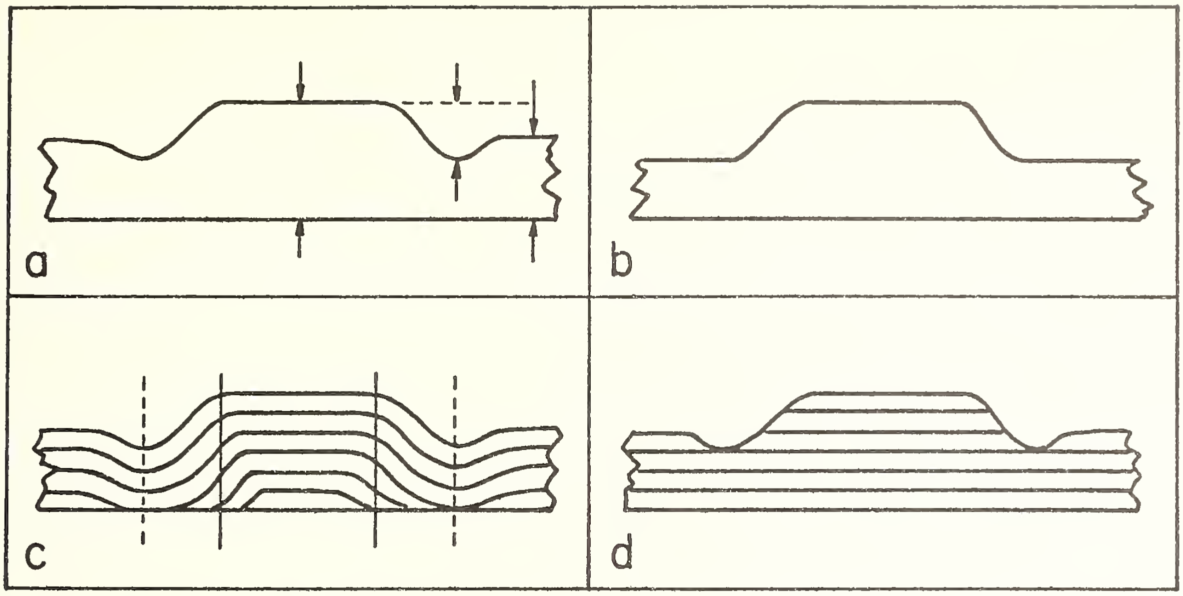


FIG. 5.—Diagrams of metal structures; cross sections.

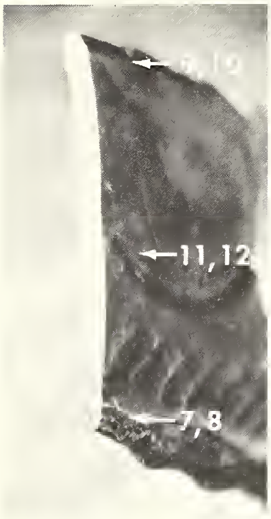


FIG. 6.—Edge-on view of the cross section of the horse's foreleg showing location of Figures 7–12. × 10

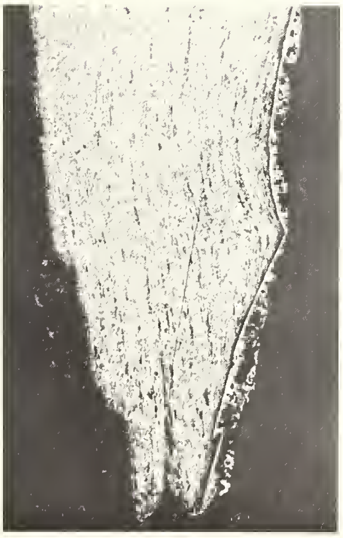


FIG. 7.—Lower edge of the leg. × 110, Dichromate etch.

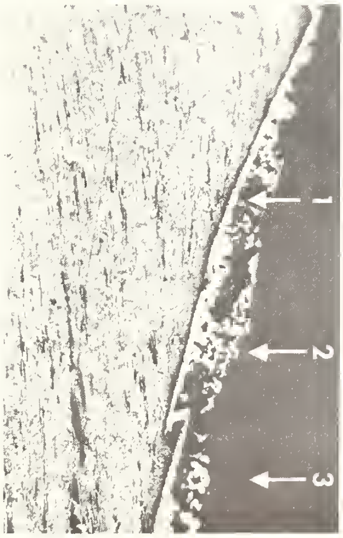


FIG. 8.—Detail of Figure 7 showing chisel strokes. × 220

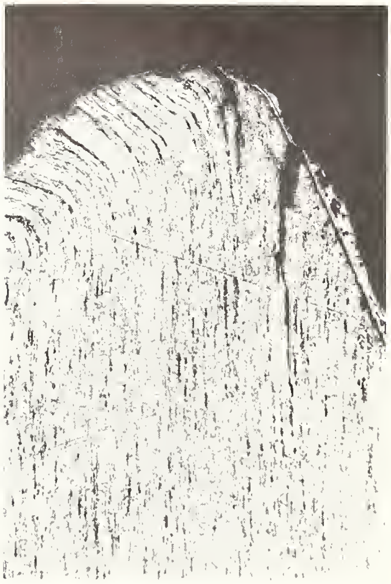


Fig. 9.—Upper edge of leg. × 110.

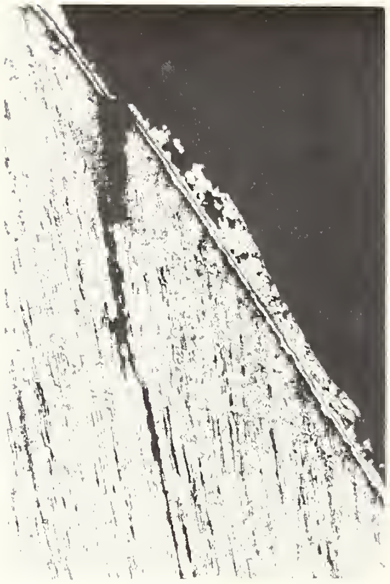


Fig. 10.—Detail of Figure 9. × 220.

Fig. 11.—Sloping contour, showing a cut off structure. × 220.

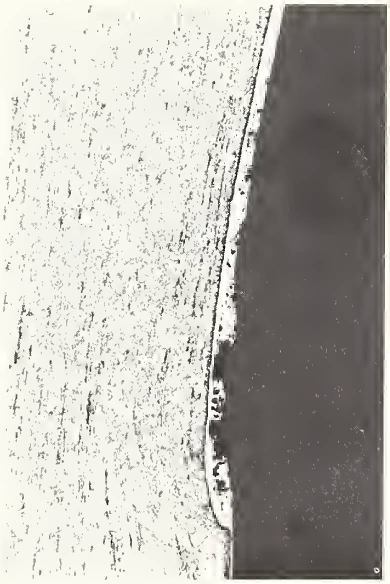


Fig. 12.—Traced decorative line showing metal flow beneath. × 110.

can be distinguished on the sloping lower edge of the leg. The silver became very thin around the contours of the leg, resulting in subsequent breaking out of the relief and loss of most of the leg.

Final decorative lines, such as the curving outline of a muscle and the short diagonal lines representing hairs on the lower edge of the leg were traced on the relief. The flow of the metal under these traced lines contrasts sharply to the cut-off appearance of the metal in other areas (figs. 11, 12).

Radiography shows that there are 16 separate inserts on the Hormizd II plate which form the high relief. In order that these inserts be retained on the plate, a lip was formed by chiseling metal up from the plate to form a ridge and an adjacent depression (fig. 13a). The Stroganoff plate in the Freer Gallery lacks an insert on the haunch of one of the boars, and the ridge and depression can be seen (fig. 14). After the insert was in place, the ridge was crimped down onto it to hold the piece securely (fig. 13b).

The second specimen (B, fig. 3) from the Hormizd II plate was taken from the crimped ridge at the breast of the horse, at the top of the break (figs. 15a, b). One may observe the reduced thickness of the plate in the depression caused by forming the ridge. After the insert was in place and crimped in position, the top surface was smoothed by scraping, as demonstrated by the cut-off flow lines in the silver (fig. 16). The actual joint between the plate and insert was finished to be as inconspicuous as possible, and the edge of the relief shape is marked by a depression in the plate itself, and is shaped in the same way as the edge of the low relief elements (fig. 17). The finished appearance of such a joint may be illustrated by a detail of the king's proper left arm (fig. 18, fig. 13c).

According to the flow lines in the metal, a bump was formed on the under side of the plate when the ridge was chiseled up and was later removed (fig. 19). It has been suggested that the original thickness of the plate may have been much greater than at present in

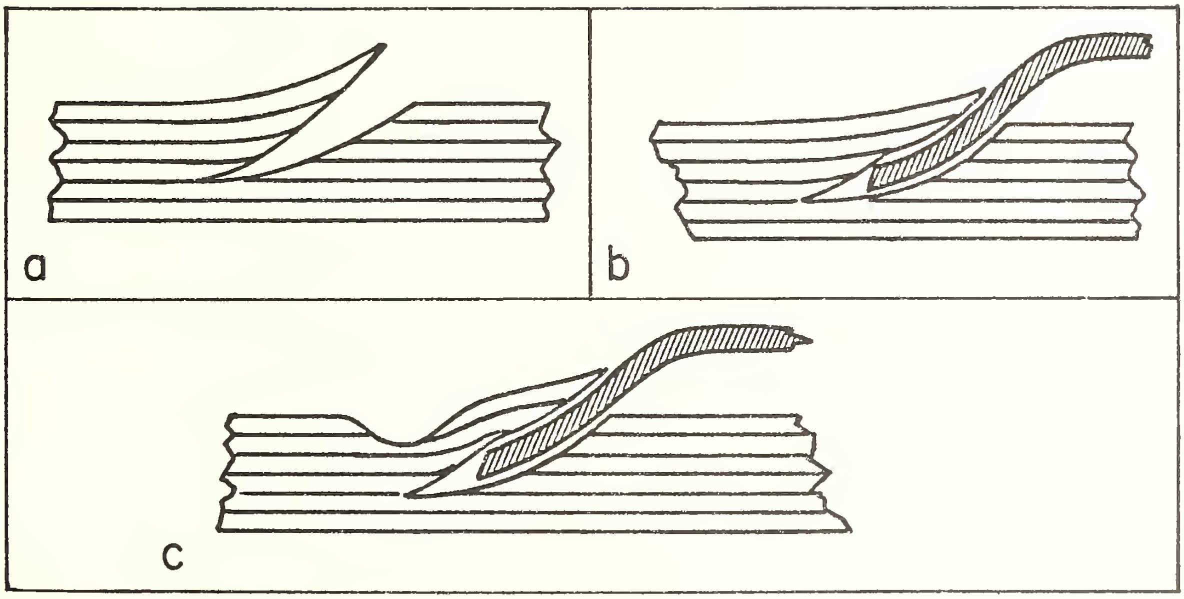


Fig. 13.—Diagrams of steps in making an insert in the plate relief.

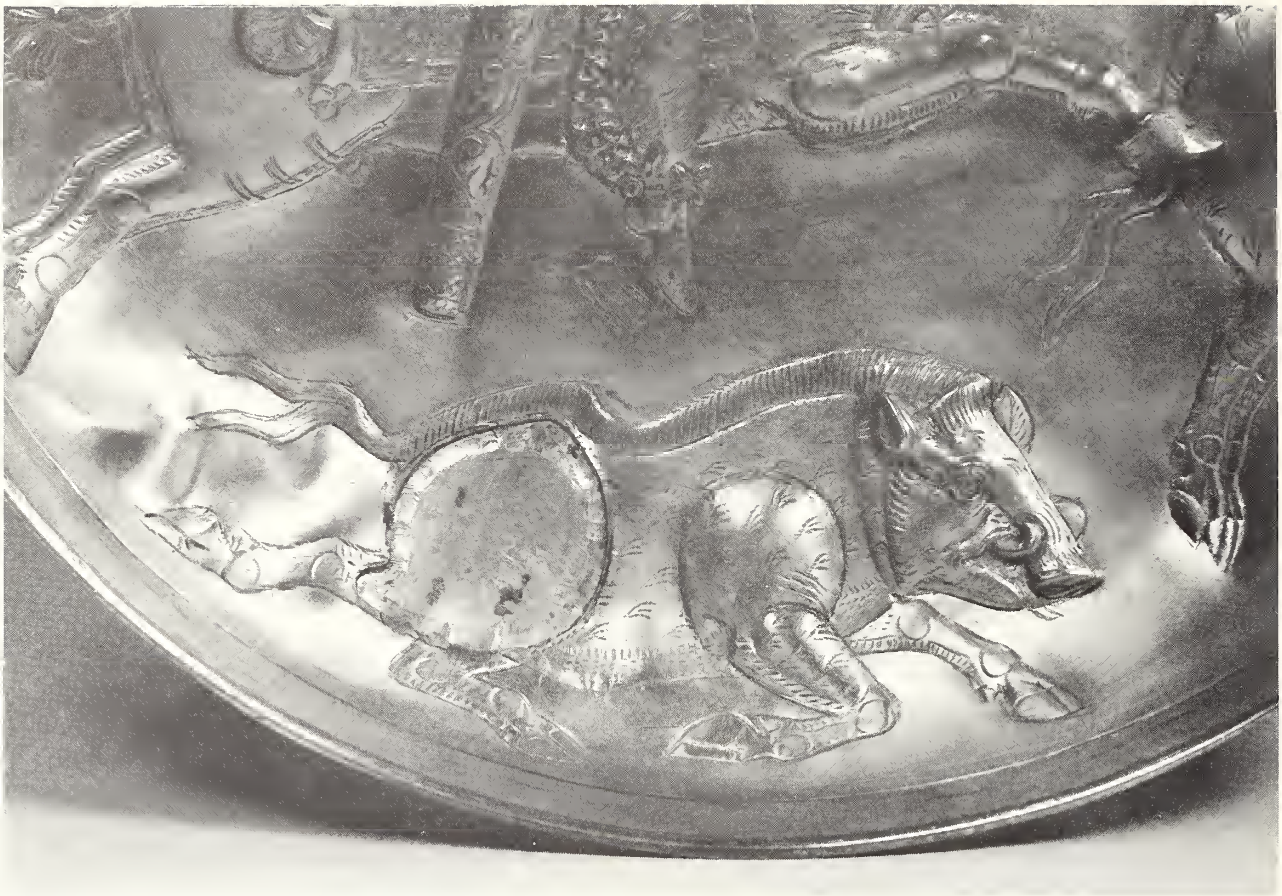


FIG. 14.—Detail from the Stroganoff plate, showing an insert missing from the haunch of the boar. Photograph courtesy of the Freer Gallery of Art, Smithsonian Institution, Washington D.C. (34.23).

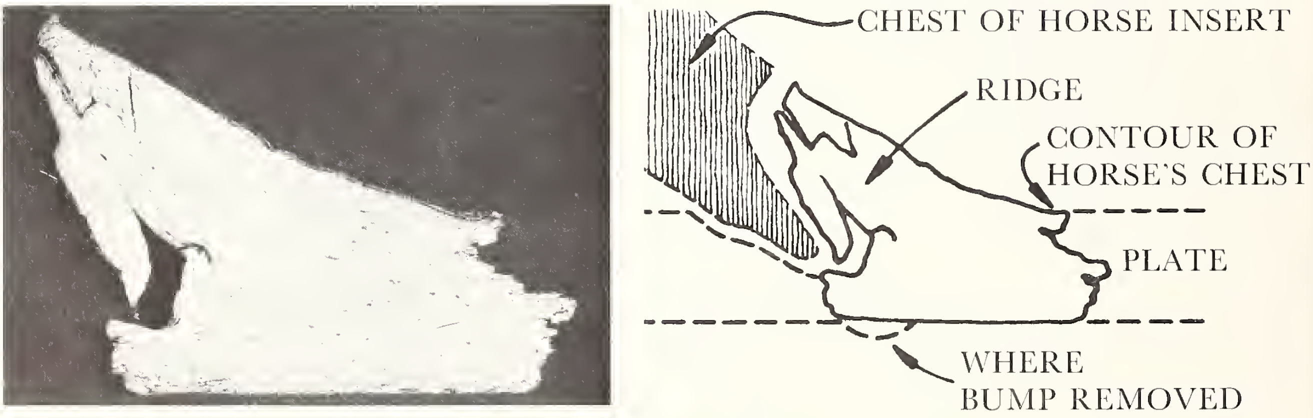


FIG. 15.—Section from the crimped ridge at the breast of the horse. × 53, Dichromate etch.

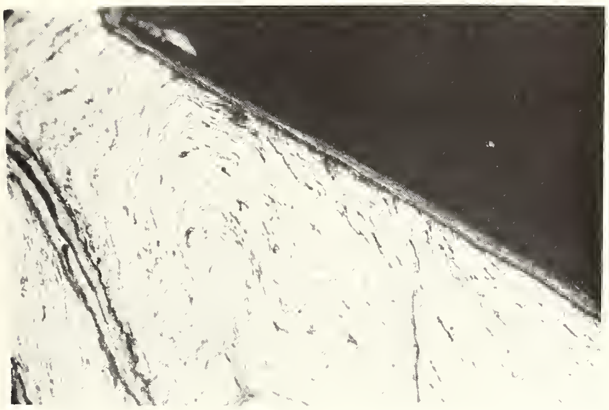


Fig. 16.—Detail of Figure 15. Top surface smoothed by metal removal. ×230.

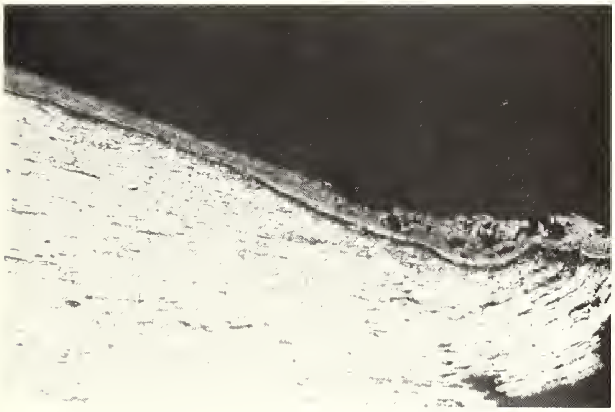


Fig. 17.—Detail of Figure 15. Smoothed surface and a depression marking the edge of the relief shape. ×230.

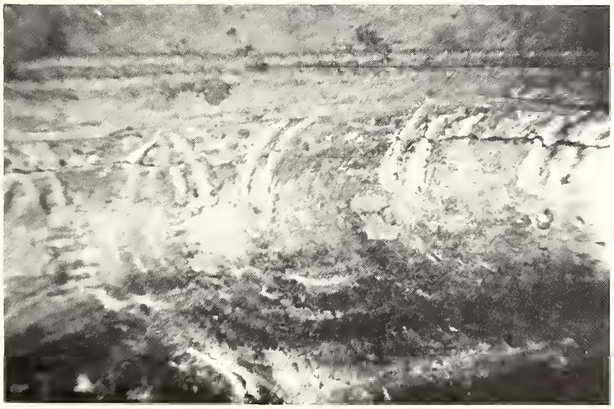
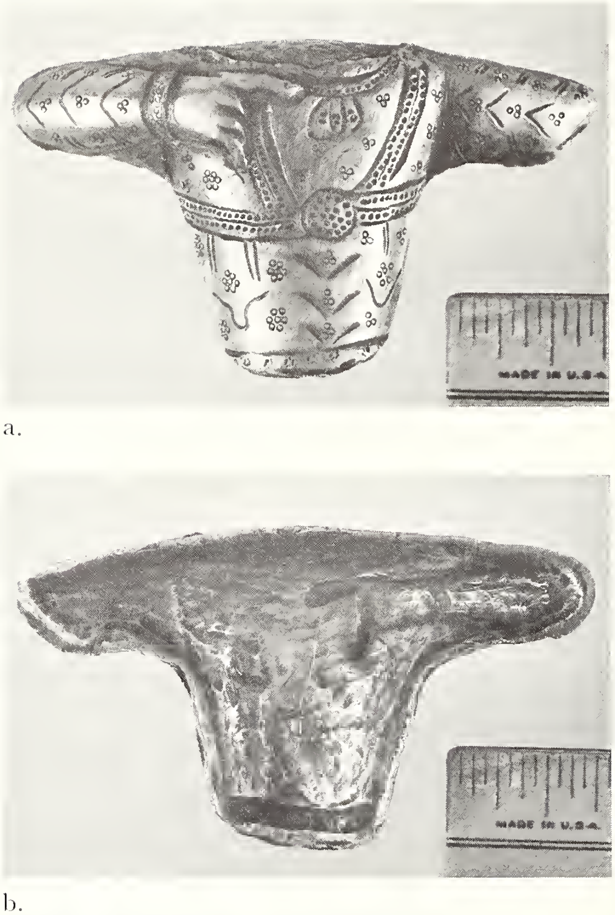


Fig. 18.—Detail of the arm of Hormizd II. ×7.6.

Fig. 19.—Detail of Figure 15. Bottom surface of the plate where a bump was removed. × 240.

order to support such a deep chisel cut with relatively little deformation in the surrounding metal. The supposition is that, after the decoration of the plate was complete, it was thinned by removing considerable metal from the back. There is no way to confirm this theory, however, without attempting to duplicate the structure observed in the specimens.

We were fortunate to obtain a separate torso of a king, an insert for another plate, which corresponds very closely to that inserted in the Hormizd II plate (figs. 20a, b). This study piece has allowed us to make some observations of techniques used in the inserts. As one can see from the back of the torso, sinking was used to block out the rough form. Probably final modeling of the outer surface was done by cutting away metal, followed by punching and tracing the linear decoration. The edges of the torso which were to be crimped down on the plate were systematically roughened to provide a mating surface which would hold the ridge firmly (fig. 21). This technique is also seen at the neck of the torso. Not only was a deep groove with a corresponding ridge formed all around the neck to receive the head insert, but the hidden



a.

b.

Fig. 20.—a. front, b. back. Torso of a king.

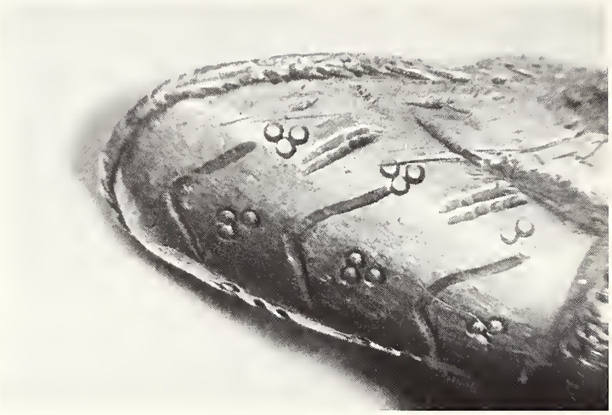


Fig. 21.—Arm, detail of Figure 20a. Note the upper edge roughened to grip a ridge. × 7.6.

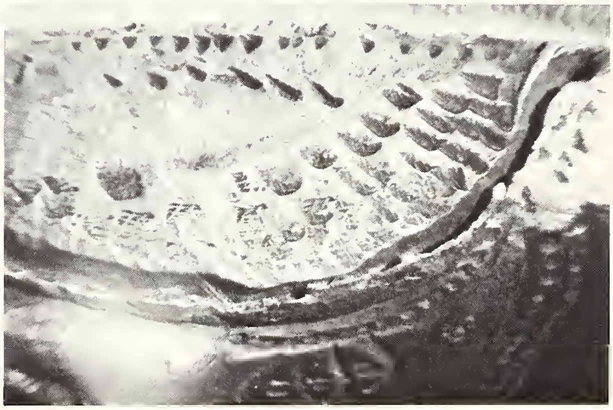


Fig. 22.—Neck area, detail of Figure 20a. × 7.6.

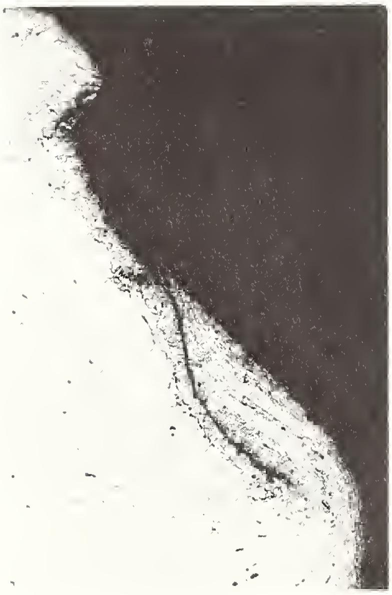


Fig. 23.—Section from the lower edge of the torso, showing the depression. × 110, Dichromate etch.

surface under the head was given a rough surface to mate with the bottom surface of the head (fig. 22).

At the bottom edge of the torso, where it once joined the lower half of the figure, we cut a metallographic section of the depression which had been shaped to receive a flange from the lower insert. No doubt the shape of this depression is similar to those formed to accept the ridge from the plate as well. Although the magnification of these two photomicrographs differs, clearly the shape of the ridge section from the Hormizd II plate (fig. 15) corresponds very closely to the depression on this torso (fig. 23) and confirms our picture of the nature of the joints between plate and insert.

It is obvious from the microstructures that both the plate and most of the inserts are wrought silver. The head of the king is, however, much more three dimensional in quality than other parts of the relief—in fact, the eagle is in full round (fig. 24). Also, this insert is more dense when radiographed. Consequently, at present, we believe that this is a cast piece, although we have no metallurgical data to confirm it.

The final steps in the production of the plate consisted of soldering the foot to the plate and finally gilding certain of the raised figures. The foot was soldered with a very fine fillet of solder and it has not been possible to obtain either chemical or metallurgical data on the solder material. The uneven boundary around the gilt figures is typical of the amalgam gilding process. The spillover of gilding onto the background is noticeable below the king's left arm and along his torso (fig. 24) as well as elsewhere. The section obtained from the crimped ridge near the breast of the horse had been gilded. Figure 25 shows a trace of the change in composition of the elements gold, mercury, copper, and silver, obtained by electron microprobe with the beam diameter of 1μ as the beam traversed from the surface inwards to a depth of 180μ. The sharp dip in gold concentration ("A", fig. 25) indicates a pore in the gilding which had not been closed by the burnishing tool. It can be seen from the presence of mercury that some still remained in the gold after firing the amalgam and also that mercury had diffused into the silver plate to a depth of approximately 15μ. The sharp decrease in silver concentration and simultaneous increase in copper concentration ("B", fig. 25) occurred as the traverse crossed a region of copper-rich eutectic. The gold and silver concentrations at the interface between the gilding and plate proper show the diffusion of silver into the gold and vice versa, which occurred during the firing of the amalgam.

A summary of the techniques used in making the Hormizd II plate is then as follows: the plate was raised from a hammered piece of silver sheet, the thickened rim probably shaped by hammering the edge back onto itself. Then, after the design was planned, the ridges for holding inserts were formed and semi-finished inserts were crimped in place. Final shaping of the outside surfaces of the inserts, and shaping of the low relief, was accomplished by removing metal from the upper surface of the plate. Metal may also have been removed from the bottom, thinning the plate. Then linear decorative elements—lines and dots—were punched and traced where desired. A round foot was soldered to the bottom of the plate. Finally, mercury amalgam gilding was applied to many of the raised portions and burnished.

A footnote to this description of Sasanian silversmithing techniques should be a word about the composition of silver. We have been

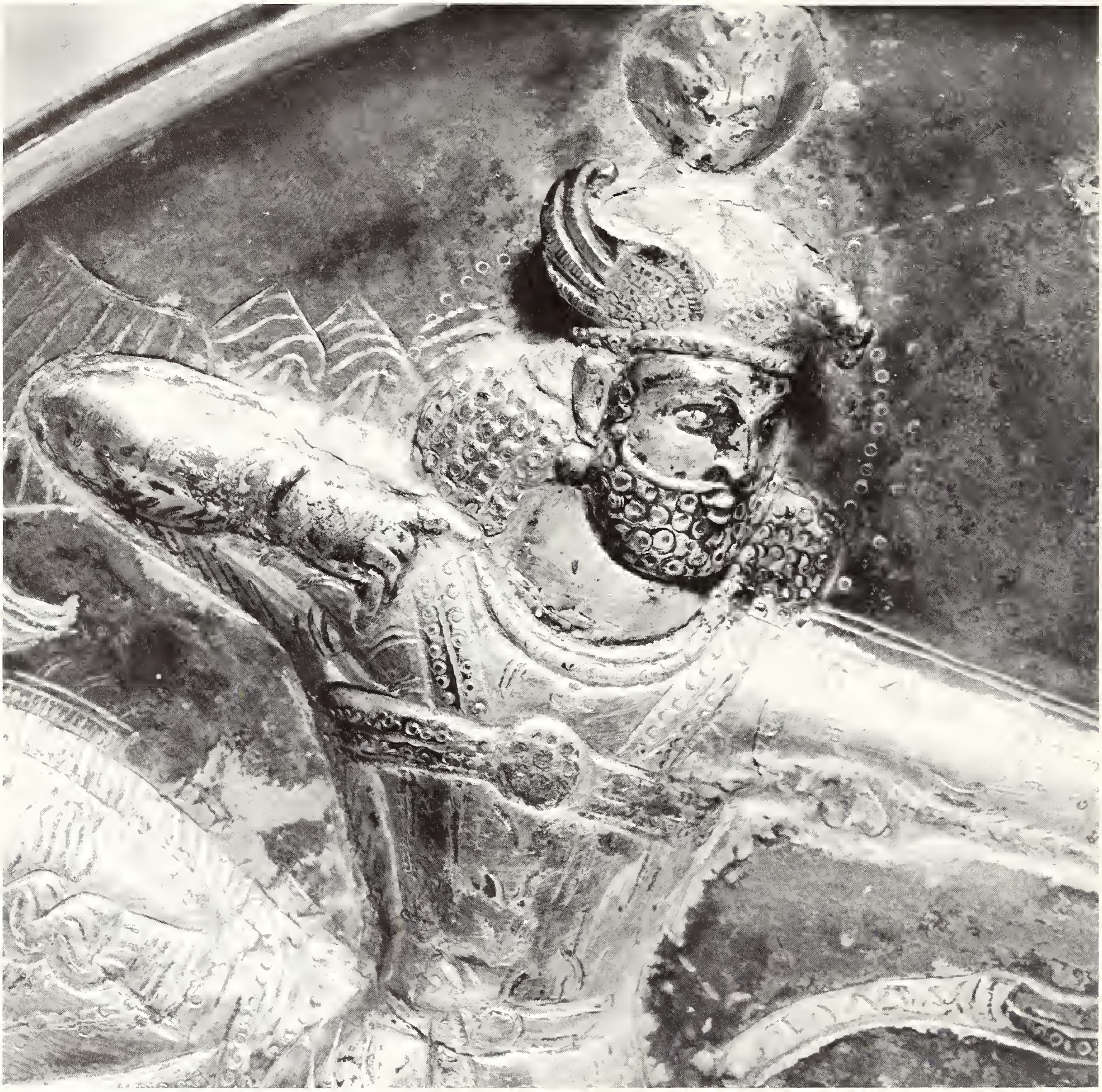


FIG. 24.—Detail of the Hormizd II plate.

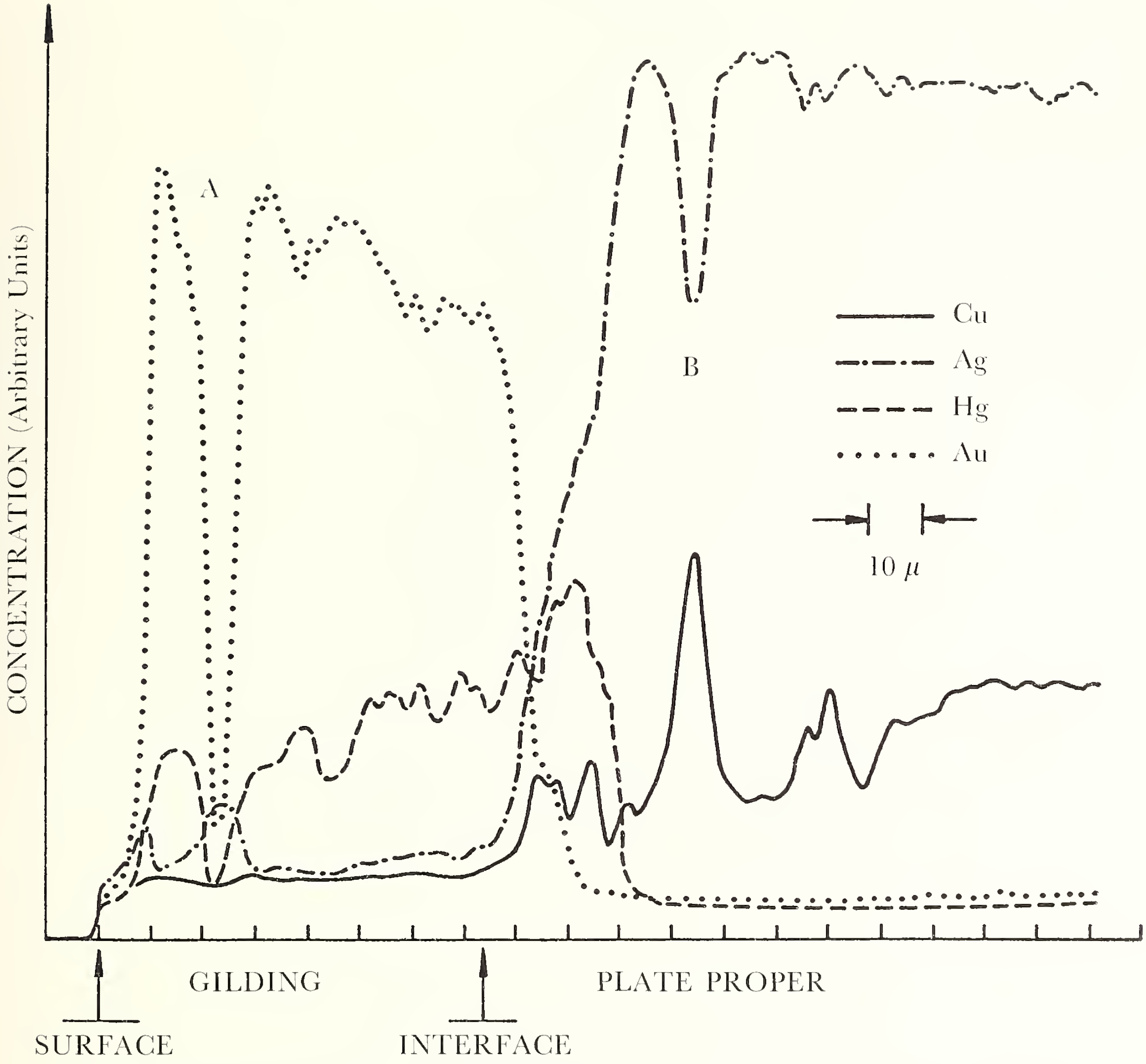


Fig. 25.—Electron microprobe trace across the gilded layer on the section from the breast of the horse.

especially interested in the copper content and have found a wide variation among the Sasanian objects examined.[5] In the objects specifically under discussion here, the torso insert has a copper content of only 0.4–0.5 percent, while the Hormizd II plate has 7–8 percent copper. This difference in composition affects the properties of the silver, both in working it and in the subsequent use of the object. We have no way of knowing whether the Sasanian silversmith appreciated or attempted to control chemical composition; he must, however, have been aware of the increased rate of work hardening as the amount of copper was increased. He certainly was conscious of work hardening during hammering and subsequent annealing to soften the metal, as all our specimens show microstructures which are the result of working and annealing cycles.

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[5] D. F. Gibbons, K. C. Ruhl and L. S. Staikoff, "Analysis of Sasanian Silver Objects: A Comparison of Techniques," *Archaeological Chemistry*, C. W. Beck ed., Advances in Chemistry Series, No. 138 (Washington, D. C.: American Chemical Society, 1974), pp. 11–21.

THE METALLURGICAL TECHNIQUE OF THE SILVER "*PLATE WITH FIGURES*," GUPTA PERIOD

By DONALD F. GIBBONS*
and KATHARINE C. RUHL*

The "Plate with Figures" in the Cleveland Museum of Art dates from the Gupta period of Indian art, 300–500 A.D. (figs. 1, a, b). A technical study was performed at the Cleveland Museum of Art and Case Western Reserve University, using visual examination at low magnifications, radiography, and metallographic examination of two small sections.

The plate is decorated with very low relief on both back and front. Traces of gilding can be discerned on the background of both the group of figures on the front and the procession of elephants just inside the rim on the back. Considerable variation in the thickness of the plate is visible by radiography (fig. 2). The metal thickness at the rim was measured as ranging from 2.5 to 3 mm. Moving towards the center of the plate it tapers to approximately 1 mm at the thinnest area immediately adjacent to the figures in relief (which corresponds on the reverse to the background at the feet of the elephants). The thickness increases slightly towards the center of the plate. Although the relief is low, it does correspond to greater metal thickness, which indicates either casting or that metal was removed or moved to create the effect. In contrast, the drapery behind the figures is very linear and is formed by a tracing technique as no change of metal thickness is detected by radiographic density.

Since a fragment is missing from the rim, one can observe the taper from the edge to the thinnest area of the plate directly. A small samples was removed from the position indicated by arrows on Figure 3 and prepared for metallography (fig. 4). The metal used for this plate, as determined by electron microprobe analysis, is composed of 55% silver and 45% copper. An alloy of this composition forms a two-phase structure of copper-rich dendrites in a silver-rich matrix. The distortion of the cast structure, demonstrated by the elongation of the copper dendrites (fig. 5), although not extensive, is enough to show that the plate was formed by working from a cast slug and not cast directly to shape. After the plate was shaped, the copper-rich phase was removed from the surface by chemical treatment to a depth of approximately one millimeter, leaving a spongy layer of silver solid solution overlying the core of silver-copper alloy (figs. 6, 7). In some areas, cracking has occurred along the interface between the layers (fig. 8), giving a multi-layered effect which may be observed by visual examination of the broken edges.

The relief decoration was then developed. The most likely technique is the mechanical removal of the silver layer from the background areas. Our section passes through the rim and part of the background of the procession of elephants (fig. 3). The silver layer, which is about a millimeter thick at the rim, diminished to almost nothing in the background area, while the thickness of the silver-copper core remains the same. Although the layer of gold is no longer present in this particular spot, the coppery color of the core metal would have been covered up by the

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* Case Western Reserve University, Cleveland, Ohio.

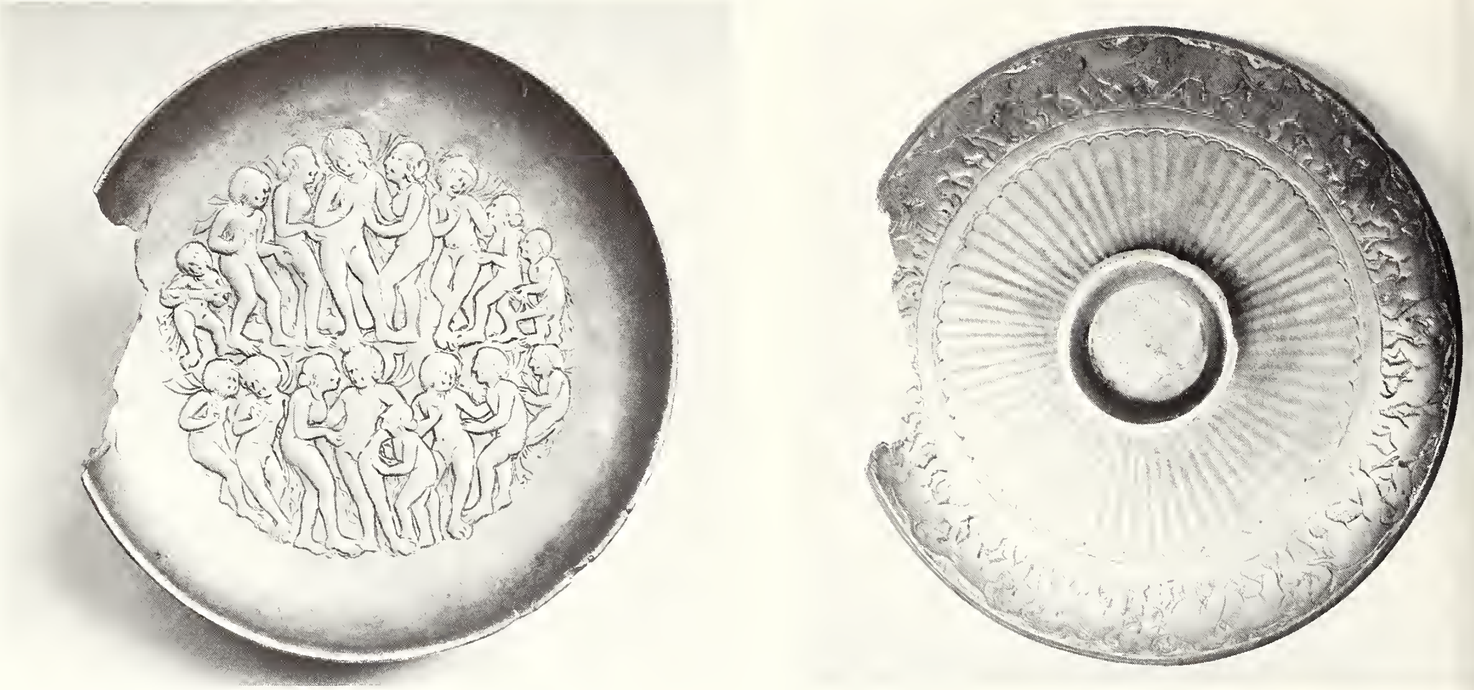
a b

Fig. 1.—a. front, b. back, the "Plate with Figures," The Cleveland Museum of Art, Purchase from the J. H. Wade Fund. 72.71.

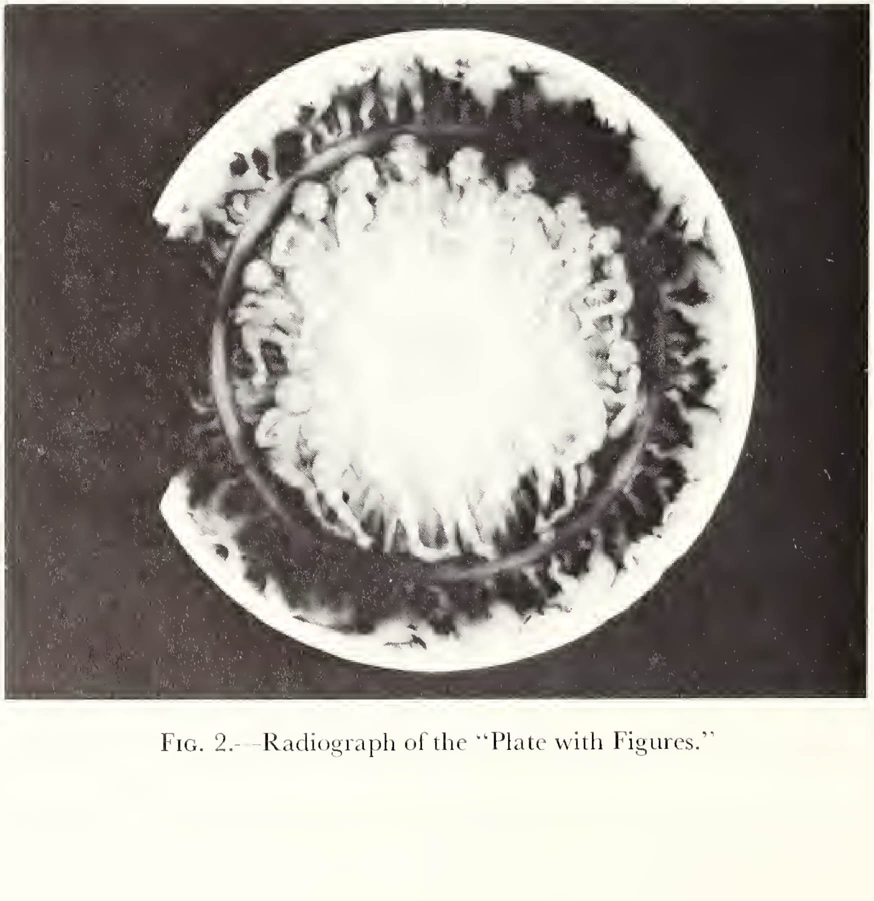

Fig. 2.—Radiograph of the "Plate with Figures."

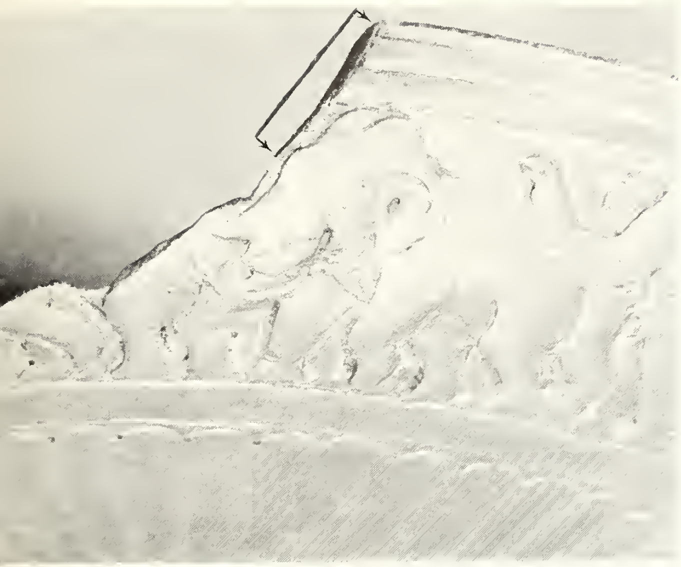

FIG. 3.—Broken area of the plate showing the location from which the metallographic section was obtained.

gilding of the background, if by chance the silver layer was totally removed in one of these areas. If the surface enrichment had been performed after the relief was developed, the thickness of the enriched layer would remain constant while that of the core metal would vary with the height of the relief, which, as noted above is not the case. Another possibility would have been to develop the relief after the surface enrichment step was completed, by consolidation of the spongy material. This would have resulted in a layer of dense silver rich material in the background areas, which again was not observed. After the relief was completed, the plate was burnished, consolidating the surface of the spongy silver into a compact layer of high silver content (fig. 9).

A low circular foot is soldered to the bottom of the plate. A section from the foot also showed a silver-copper alloy of a composition and structure similar to the main body of the plate. The section passes through an area in which the copper-rich phase has been entirely removed. Consolidation of the surface is again evident (fig. 10).

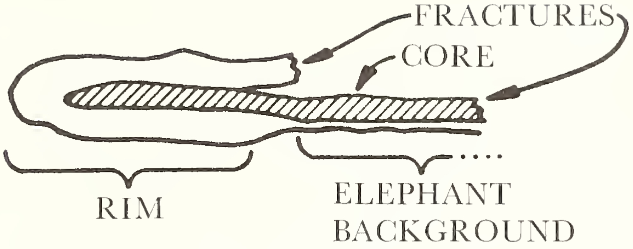

FIG. 4.—Diagram of the metallographic sample.

The ingenious use of the silver-copper alloy with the technique of surface enrichment made it possible to produce a very thin plate which has both the strength and stiffness of a copper-rich alloy and the surface appearance of pure silver.

The technique for surface enrichment of silver alloys has also been used on coins[1] where it has usually been assumed that the intent was to utilize debased silver.

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[1] L. H. Cope, "Surface-silvered Ancient Coins," *Methods of Chemical and Metallurgical Investigation of Ancient Coinage*, E. T. Hall and D. M. Metcalf, eds., (London: Royal Numismatic Society Special Publication No. 8, 1972), p. 261.

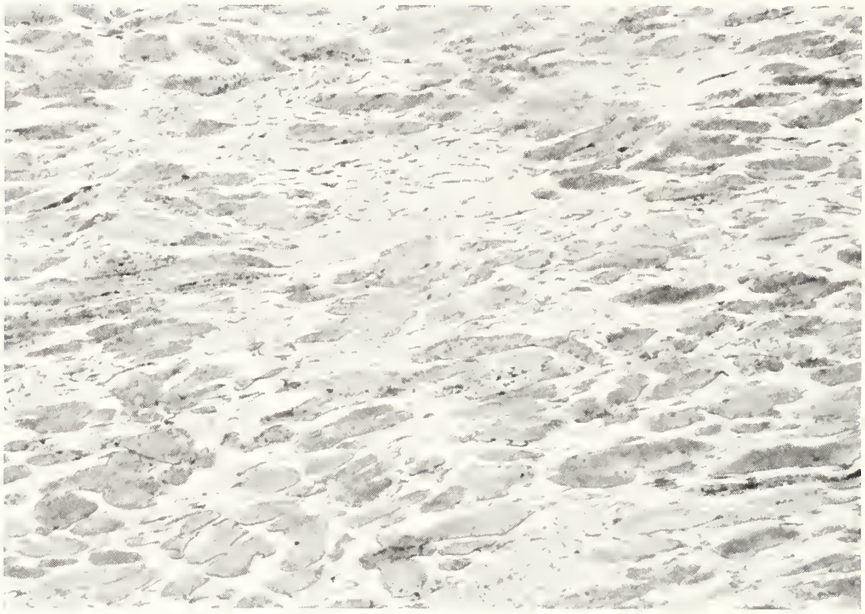

FIG. 5.—Structure of the cast and deformed copper-silver alloy (×400, etched with chromic acid-sulphuric acid reagent).

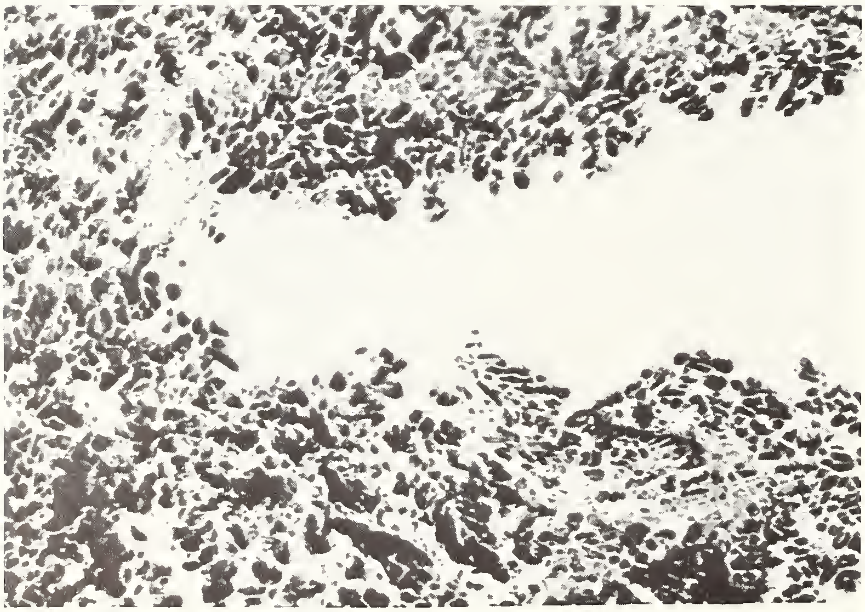

FIG. 6.—The layer of spongy silver-rich metal surrounding the core of copper-silver alloy at the rim (×100, unetched).

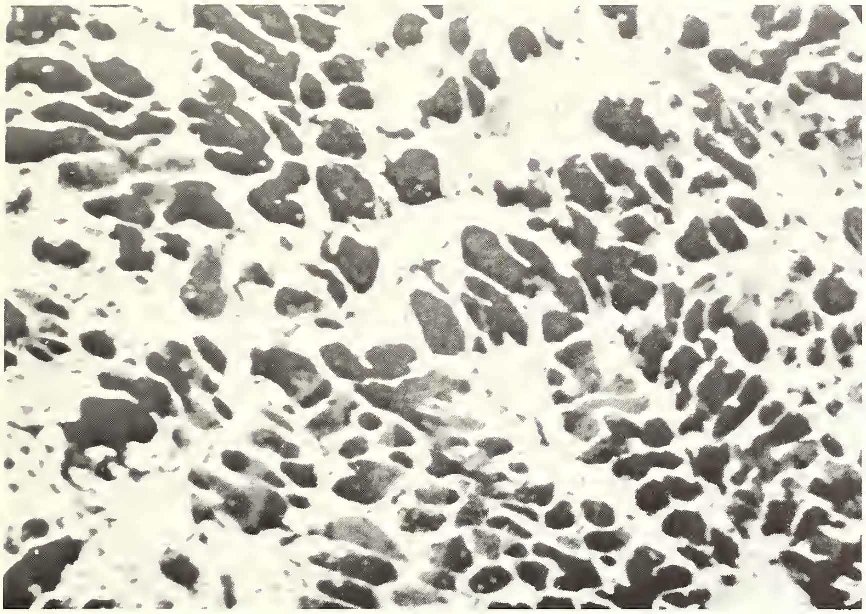

FIG. 7.—Detail of the silver-rich solid solution with the copper-rich phase removed (×400, unetched).

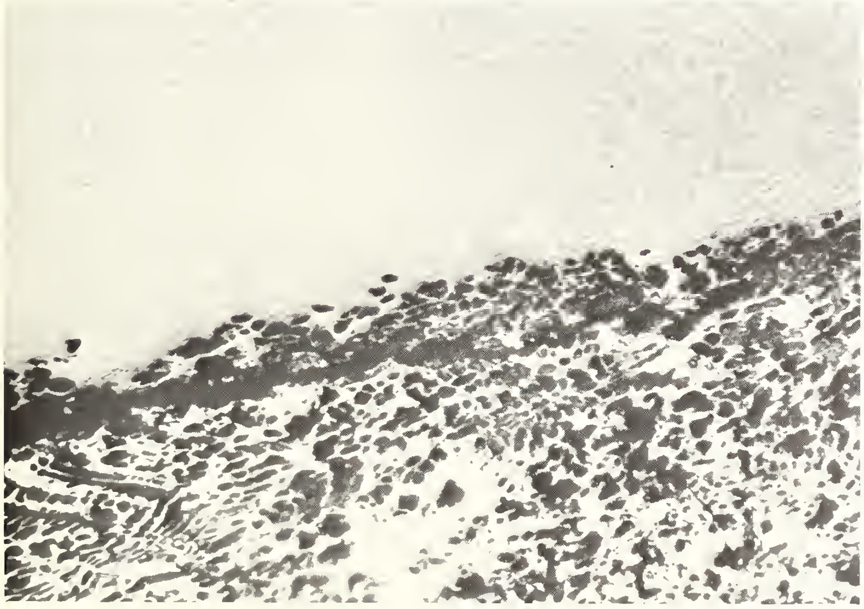

FIG. 8.—Crack at the interface between the layers of metal (×100, unetched).

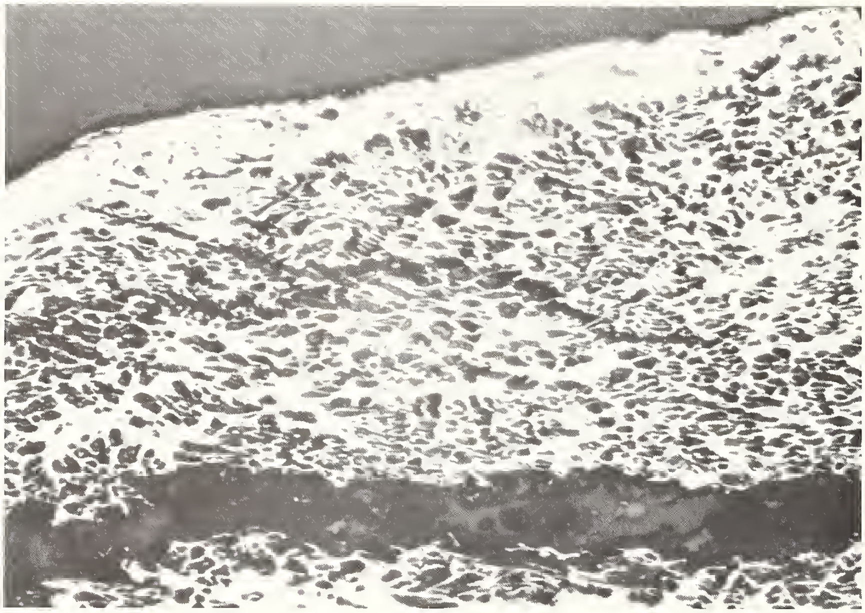

FIG. 9.—Consolidated surface of the silver-rich layer. The black zone at the bottom is a crack. (×100, unetched).

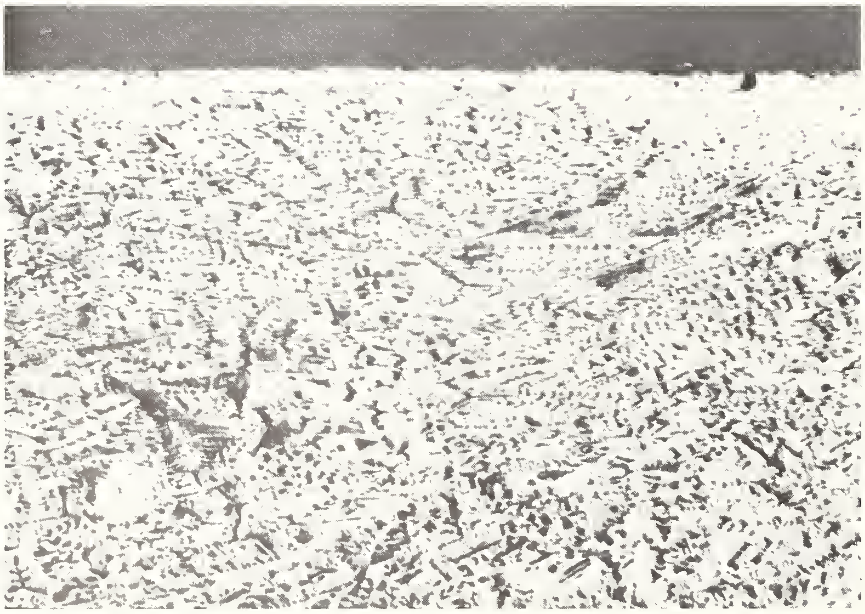

FIG. 10.—General appearance of the section from the foot of the plate, showing the consolidated silver at the surface (×100, unetched).

GRAVIMETRIC AND SPECTROGRAPHIC ANALYSIS OF SOME ANCIENT CHINESE COPPER ALLOYS

By EARLE R. CALEY*
IN SOON MOON CHANG*
AND NILUFER PARANYI WOODS*

In 1957 John Gettens submitted for analysis 14 metal specimens selected from the study material available at the Freer Gallery. As is shown in Figures 1–4, they were fragments of a variety of objects except for two intact examples of knife money and spade money. Their assigned numbers and various items of information about them are given in the figure captions. The results of quantitative analyses of samples prepared from these specimens are now reported and discussed.

The analyses were done by two graduate students in the Department of Chemistry of the Ohio State University under the supervision of Earle R. Caley. Mrs. In Soon Moon Chang analyzed 30 samples gravimetrically, and her results are the subject of a thesis[1] she submitted in partial fulfillment of the requirements for the M.S. degree. Mrs. Nilufer Paranyi Woods examined by emission spectrography a like number of samples for minor and trace elements, and her findings constitute a portion of a thesis[2] she submitted in partial fulfillment of the requirements for the same degree.

PREPARATION OF SAMPLES FOR ANALYSIS

The original surfaces and some of the broken surfaces of the specimens were coated with corrosion products that varied much in thickness. By means of files and other hardened steel tools these were removed entirely from the smaller specimens and from those parts of the larger specimens that were to be sampled. For gravimetric analysis, pieces of bare metal weighing not less than 0.8 gram nor more than 1.2 grams were cut from the cleaned specimens with a hardened steel chisel. Much smaller samples were removed for spectrographic analysis.

ANALYTICAL METHODS

The procedures employed for the chemical separation and gravimetric determination of the elements in the samples are described in detail elsewhere.[3] With the exceptions noted later on, two independent samples taken from each specimen were analyzed gravimetrically. The spectrographic determinations were made in duplicate or replicate by Harvey's method using an Applied Research Laboratories 1.5 meter spectrograph,[4]

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* Department of Chemistry, The Ohio State University, Columbus, Ohio.

[1] In Soon Moon Chang, *Chemical Composition of Some Ancient Chinese Alloys*, M. S. Thesis, The Ohio State University, 1957. Unpublished, not available on microfilm.

[2] Nilufer Paranyi Woods, *Applications of Spectrographic Methods in Archaeological Chemistry*, M. S. Thesis, The Ohio State University, 1963. Unpublished, not available on microfilm.

[3] Earle Radcliffe Caley, *Analysis of Ancient Metals* (Oxford: Pergamon Press, 1964), pp. 81–90.

[4] Charles Eugene Harvey, *A Method of Semi-Quantitative Spectrographic Analysis* (Glendale, California: Applied Research Laboratories, 1947).

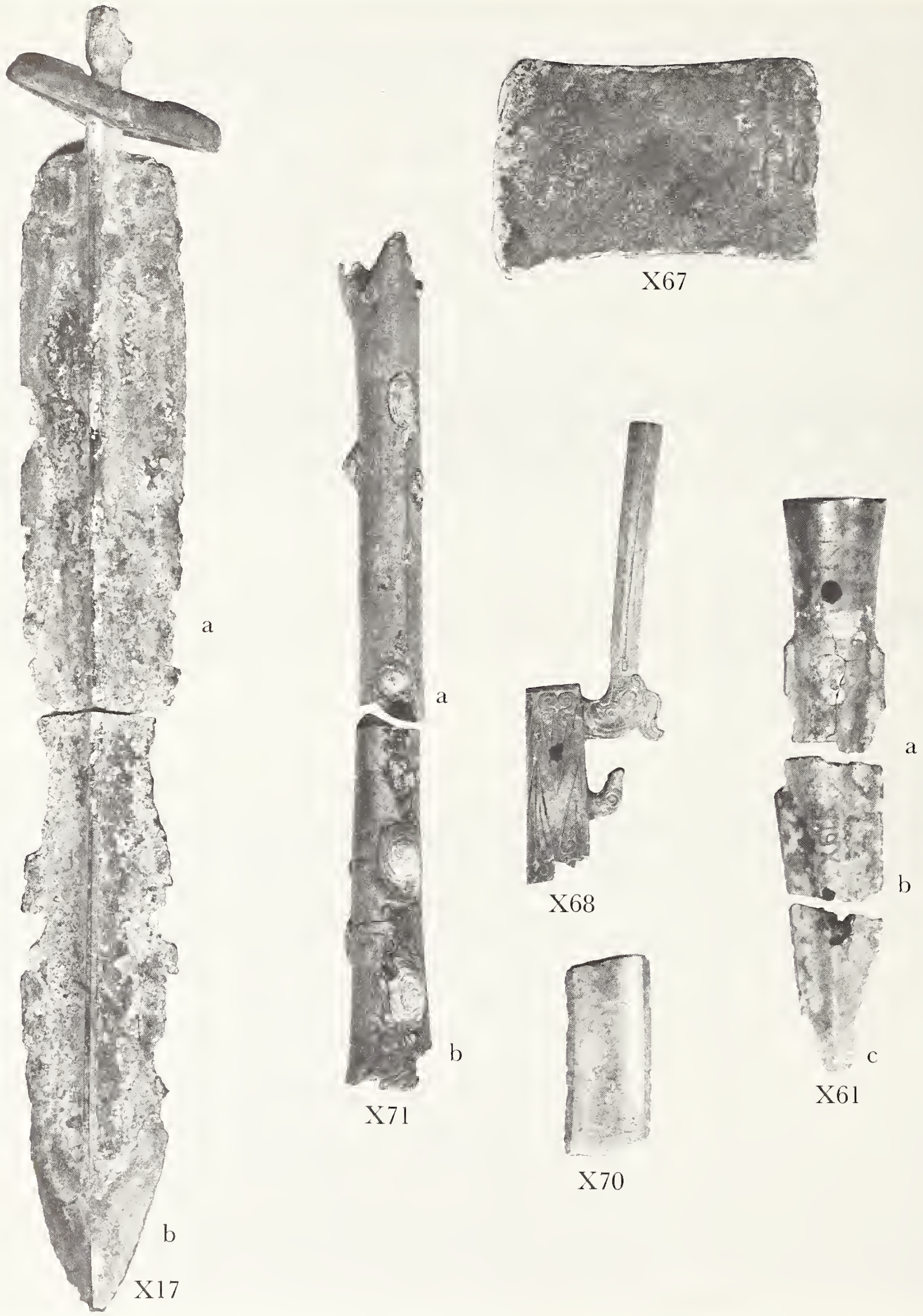

Fig. 1.

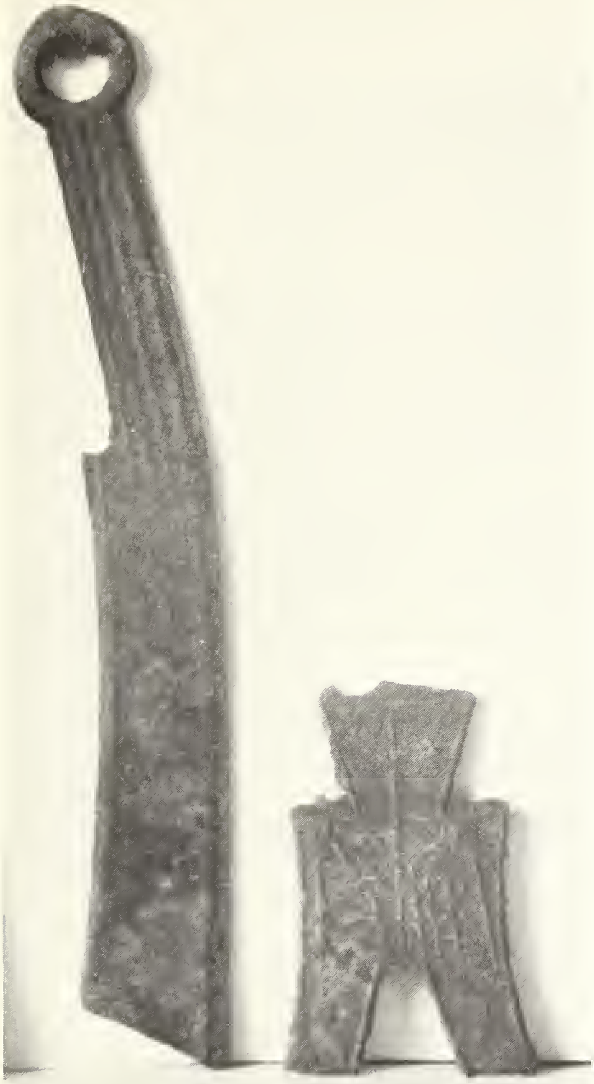

Fig. 2.—X201, Knife money (left). Weight, 17.3 grams. X204, Spade money (right). Weight, 5.9 grams.
Chou Dynasty (1028–256 B.C.) Freer Gallery of Art, Bishop Collection. Natural size.

Fig. 1.—Fragments of various objects X17, Dagger. Fragment *b* submitted for analysis. Weight, 15.0 grams. X61, Spear. Fragment *a* submitted for analysis. Weight, 15.0 grams. X67 Celt. Weight, 9.5 grams. X68, Chariot fitting(?). Weight, 8.7 grams. X70 Blade. Weight, 6.8 grams. X71, Handle(?). Fragment *a* submitted for analysis. Weight, 14.0 grams. All the above date from the Chou Dynasty (1028–256 B.C.) or earlier. Freer Gallery of Art, Bishop Collection, 0.9X. Not illustrated is F130A, a piece from the rim of a ceremonial vessel (*p'ou*), F.G.A. 13.30. Weight, 5.2 grams.

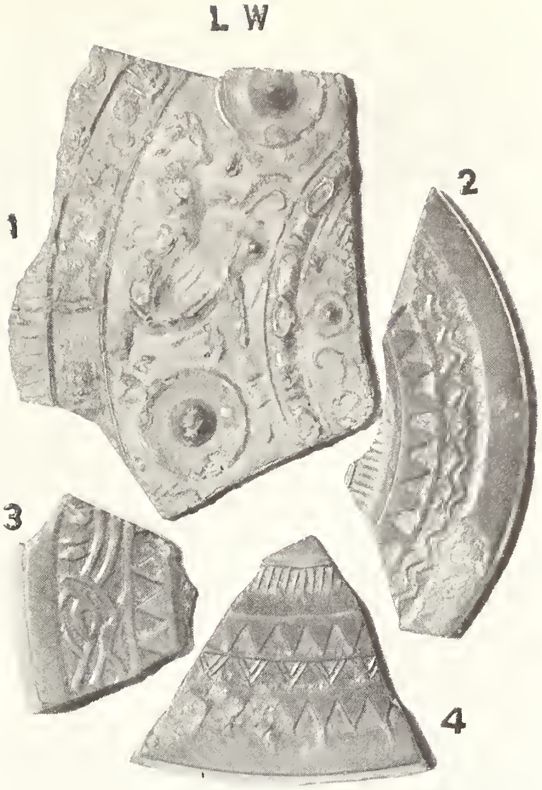

Fig. 3.—Fragments of Mirrors LW1, LW2, LW3, and LW4 with respective weights of 9.0, 4.3, 4.1, and 3.7 grams.
Han Dynasty (256 B.C.–220 A.D.) Gift of Langdon Warner. × 1.5.

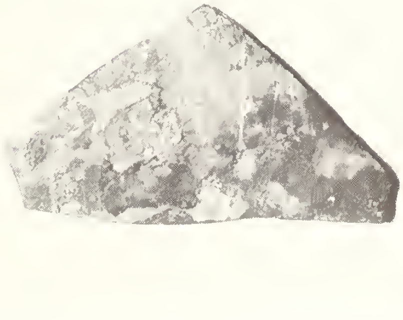

Fig. 4.—LW5, Fragment of Mirror (observe and reverse). Weight 6.4 grams.
Han Dynasty (256 B.C.–220 A.D.) Gift of Langdon Warner. Natural size.

the specific experimental conditions being as follows:

Current: A.C. with nine-ampere arc
Electrodes: Spectrographic carbon
Slit width: 30 microns
Wavelength range: 2130–4350 Angstroms
Exposure time: 60 seconds
Film type: Spectrum analysis No. 1
Developer: High contrast D-19

The intensities of the spectral lines on the developed films were measured with an Applied Research Laboratories Densitometer-Comparator.

Both spectrographic analysis and a volumetric method were used for the determination of antimony in samples from specimens X201 and X204, but the results obtained by the volumetric method were accepted as more accurate because of the relatively high proportions of this element present in these samples. In this method the residue left from the nitric acid treatment of a sample was filtered off and washed in the usual way. Both residue and filter paper were then completely dissolved by heating in a mixture of eight milliliters of concentrated nitric acid and five milliliters of concentrated sulfuric acid containing two grams of ammonium persulfate. After cooling, seven milliliters of concentrated hydrochloric acid, seven milliliters of water, and half a gram of sodium sulfite were added. The solution was then boiled until all the sulfur dioxide was expelled. After diluting with 200 milliliters of water and cooling to about 10°C, the solution was titrated with a potassium permanganate solution that had been standardized against pure antimony by the same procedure.

DISCUSSION OF ANALYTICAL DATA

The percentages of copper, tin, lead, zinc, and nickel, and also the percentages of silver

TABLE 1

Analyses of Fragments of Various Objects

No.	Cu %	Sn %	Pb %	Zn %	Fe %	Ni %	Co %	As %	Sb %	Bi %	Ag %	Total %
X17b	79.31	15.85	3.82	0.35	none	none	none	0.44	0.07	0.03	0.002	99.96
	79.72	15.81	3.63									
X67	85.62	13.71	0.07	none	0.007	0.20	trace	none	none	0.03	0.002	99.65
	85.29	14.06	0.07									
X71a	79.21	19.22	0.27	0.14	0.03	0.15	none	0.45	0.08	0.07	0.10	99.65
	78.94	19.27	0.32									
F130A	79.94	19.45	0.24	none	0.14	none	none	0.08	trace	0.04	0.003	99.92
	80.24	19.21	0.23									
X61a	69.07	19.72	9.51	none	none	none	0.003	0.33	0.03	0.08	0.09	99.85
	69.80	18.96	9.57									
X68	69.46	17.38	12.10	none	0.009	0.12	trace	none	0.01	0.07	0.10	99.30
	69.41	17.64	11.97									
X70	68.11	16.59	13.18	none	none	0.10	0.003	0.65	0.04	0.06	0.002	99.63
	68.75	16.58	12.31									

in X71a, X61a, and X68, shown in Table 1 were determined gravimetrically. All others were estimated by spectrography. The totals of the averaged duplicate analyses are satisfactory for X17b, F130A, and X61a, less so for X67, X71a, and X70, and much less so for X68. The low total for X68 may be due to the presence of undetermined nonmetals contained in internal corrosion products.

Since low percentages are unreliable indices of precision, only the individual results of the duplicate determinations of copper, tin, and lead are listed in Table 1, and of these the percentages of lead below 1% should be excluded from consideration. Of the others, the percent difference between the pairs is less than 0.25 for six, between 0.25 and 0.50 for six, and more than 0.50 for four. The four pairs that seem to indicate the poorest precision are the percentages of copper in X61a and X70, the percentage of tin in X61a, and the percentage of lead in X70. Although this apparent poor precision might seem to be the results of analytical error, the sum of the percentages of copper, tin, and lead in the individual analyses of X61a and X70 indicate otherwise. For X61a this sum is 98.30% for the first analysis and 98.33% for the second, and for X70 the respective sums are 97.88% and 97.64%. What appears to be poor precision may actually be an indication that the samples for each pair of analyses were of different composition due to a lack of homogeneity in the metal.

The percentages of copper, tin, lead, zinc, nickel, and sulfur shown in Table 2, as well as the percentages of arsenic in X201 and X204, and the percentages of silver in LW2, LW3, and LW4, were determined gravimetrically. The percentages of antimony in X201 and X204 were determined volumetrically. All others were estimated by spectrography. The totals are satisfactory

TABLE 2

Analyses of Knife Money, Spade Money, and Mirror Fragments

No.	Cu %	Sn %	Pb %	Zn %	Fe %	Ni %	Co %	As %	Sb %	Bi %	Ag %	S %	Total %
X201	46.81	3.17	45.62	none	0.63	0.19	0.006	1.02	0.93	0.52	0.002	0.42	99.76
	47.20	3.03	45.66										
	47.60	2.00	46.11										
	47.65	3.05	46.24										
X204	58.24	0.99	32.34	none	0.18	0.12	0.005	0.40	5.84	0.17	0.001	0.26	98.39
	58.80	1.12	31.32										
LW1	69.14	25.89	4.08	none	0.05	0.10	0.003	0.07	0.08	0.04	0.008	—	99.74
	69.26	26.06	4.33										
LW2	67.63	27.19	4.55	none	0.06	0.09	0.003	0.05	0.09	0.03	0.10	—	99.75
	67.93	26.82	4.54										
LW3	70.52	24.92	4.26	none	0.09	0.05	none	trace	trace	0.08	0.05	—	99.97
	69.17	26.77	3.74										
LW4	67.79	27.00	4.67	none	0.06	0.11	0.003	trace	0.12	0.07	0.09	—	100.06
	68.90	26.10	4.75										
LW5	67.40	25.56	6.77	none	0.09	0.33	none	0.06	0.08	0.05	0.006	—	100.08
	67.47	25.56	6.14										

except for that of X204, which is very low. This low total is certainly due to the presence of internal corrosion products, which were visible when the samples were being prepared and could not be completely removed.

The replicate determinations of copper, tin, and lead in X201 and the duplicate determinations of copper and lead in X204 are in poor agreement. Here again, the cause is probably not analytical error but differences in the composition of the samples. In cast copper alloys containing such very high proportions of lead nearly all of this component is irregularly distributed as globules of metallic lead in a copper matrix. In other words, such alloys are fundamentally heterogeneous, and it is difficult to obtain several samples of identical composition.

The agreement is also poor for some of the pairs of determinations of principal components of the mirrors, namely the percentages of copper and tin in LW3 and LW4, and the percentages of lead in LW5. Here again, the basic cause is probably heterogeneity of the alloy. What all these examples of discrepancies in Tables 1 and 2 indicate is that single analyses of samples weighing even as much as one gram cannot be relied upon to yield exact results for the average composition of ancient Chinese alloys.

THE MAJOR COMPONENTS

As is shown in Table 1, the metal of three of the specimens, X67, X71a, and F130A, contained only copper and tin as major components. The proportion of tin in X67 is not much higher than that found in ordinary tin bronze, but the proportions in the other two are clearly high enough to classify the alloys as high-tin bronzes. In addition to containing high proportions of tin, the metal of X17b, X61a, X68, and X70, especially the last three, contains lead in considerable proportion. The alloys of these four specimens may be termed leaded high-tin bronzes. As is shown in Table 2, X201 was found to contain copper and lead in nearly equal proportion, with tin present in small proportion. Copper and lead are also the major components of X204 but in different proportion, and with an even smaller proportion of tin. The copper-lead alloys of these two specimens are not bronzes in the usual sense of this term. Specimens LW1, LW2, LW3, LW4, and LW5 were found to have nearly the same composition. The proportions of the major components are those of the eutectic alloy of copper and tin in which lead has replaced some of the copper. Such an alloy may be termed a leaded high-tin bronze, but speculum metal is perhaps a better term.

MAJOR COMPONENTS REPORTED IN PREVIOUS ANALYSES

An exact comparison of the present analyses with any published earlier is only possible for one of the specimens, F130A. Gettens[5] published the analysis of an adjacent piece from the rim of the same ceremonial vessel FGA 13.30. For this specimen the averaged gravimetric results obtained on samples weighing a tenth of a gram are reported as 81.9% copper and 17.8% tin. The lead content measured spectrographically is stated to be 0.3%. For F130A the averaged

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[5] Rutherford John Gettens, *The Freer Chinese Bronzes* (Washington: The Freer Gallery of Art, Smithsonian Institution, 1967–1969), vol. 2, pp. 39–53.

Table 3

Analyses of Knife Money, Spade Money, and Mirrors Reported by Chikashige

No.	Object	Cu %	Sn %	Pb %	Zn %	Fe %	Ni %	As %	Sb %	Ag %	Total %
1	Knife Money	38.38	1.66	55.41	—	2.66	1.03	0.60	—	none	99.74
2	Knife Money	45.93	2.12	48.60	—	none	1.63	1.72	—	none	100.00
3	Knife Money	42.25	2.12	47.32	—	none	5.08	3.28	—	none	100.05
4	Knife Money	46.22	9.25	43.53	—	0.73	none	none	—	0.27	100.10
5	Knife Money	64.65	6.76	21.25	—	0.41	3.04	3.88	—	none	99.99
6	Spade Money	70.42	9.92	19.30	—	none	0.35	—	—	—	99.99
7	Spade Money	65.86	14.60	14.00	—	0.41	none	—	—	—	94.87
8	Mirror	66.67	26.57	5.29	0.20	0.81	0.63	none	none	none	100.17
9	Mirror	62.15	26.47	5.29	5.00	none	none	none	1.08	trace	99.99
10	Mirror	65.10	25.07	9.12	0.16	0.06	none	trace	trace	none	99.51
11	Mirror	70.11	24.28	5.59	none	0.22	none	none	none	trace	100.20

gravimetric results on samples weighing around a gram are 80.09% copper, 19.33% tin, and 0.24% lead. Although the results of the two analyses differ somewhat, they agree as well as could be expected in view of the very different weights of the samples.

For comparison of the analyses of the other specimens with earlier analyses, those published by Chikashige[6] seem most suitable. In spite of differences in type and uncertainties as to period, the ancient Chinese hand weapons analyzed by Chikashige seem comparable in composition to specimens X17b, X61a, and X70. The tin content of seven halberds and swords analyzed by him ranges from a low of 12.55% to a high of 23.11% with an average of 16.88%, whereas the tin content of X17b, X61a, and X70 ranges from a low of 15.81% to a high of 19.72% with an average of 17.26%. Also the lead content of these halberds and swords ranges from none to a high of 11.86% with an average of 6.11%, whereas the lead content of X17b, X61a, and X70 ranges from a low of 3.63% to a high of 13.18% with an average of 5.34%. Furthermore, both groups contain examples of a high tin content coupled with a low lead content and of a high tin content coupled with a high lead content. In a general way these new analyses confirm what is already known about the proportions of the major components in the bronze of ancient Chinese weapons.

Chikashige's analyses of knife money, arranged in order of decreasing proportions of lead, are listed in Table 3. When the proportions of copper, lead, and tin found in specimen X201 (Table 2) are compared with those listed in Table 3, it will be seen that these proportions agree fairly well with those of No. 2 and No. 3 of Table 3, but not with those of the other three analyses. However, it is evident that the proportions of the major components of specimen X201 fall into the same general pattern of composition as the examples of knife money analyzed by Chikashige.

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[6] Masumi Chikashige, "The Composition of Ancient Eastern Bronzes," *Journal of the Chemical Society* (London), vol. 117 (1920), pp. 917–922; *Alchemy and Other Chemical Achievements of the Ancient Orient* (Tokyo: Rokakuho Uchida, 1936), pp. 55–83.

The two analyses of spade money reported by Chikashige (Table 3) differ considerably from each other, and from the analysis of specimen X204 (Table 2). One unusual feature in the composition of X204 is the presence of nearly six percent antimony, a proportion that might well be regarded as enough to count antimony among the major components of the alloy. Additional analyses of spade money are needed before any conclusion can be reached about the compositional pattern of this type of object.

Chikashige's analyses of Han mirrors are shown in Table 3. On comparing the proportions of copper, tin, and lead in specimens LW1, LW2, LW3, LW4, and LW5 (Table 2) with those listed in Table 3, it will be seen that these proportions agree fairly well with those of No. 8 and No. 11 of this table, and also with No. 9 if the zinc in this example is considered an accidental impurity associated with the copper. It is evident on the whole that the major components of LW1, LW2, LW3, LW4, and LW5 fall into the same general pattern of composition as those analyzed by Chikashige.

THE MINOR COMPONENTS

The most extensive investigation on the nature and proportion of the minor components of ancient Chinese bronzes was published by Gettens.[7] All the measurements reported by him were made by means of emission spectrography. In the present investigation some of the minor components were determined by accurate gravimetric methods and others were estimated by a spectrographic procedure that is a little less approximate than the one used by Gettens. The extent to which the results obtained in these two investigations agree or disagree should be of some interest. Although Gettens' results were all obtained on the metal of ceremonial vessels, this should not invalidate the comparison, for the metal of this class of objects was very probably smelted from the same kinds of ores as the metal of other classes of bronze objects.

Zinc. Chemical tests and spectrography failed to show the presence of zinc in most of the specimens, but Nos. X17b and X71a (Table 1) were found by gravimetric analysis to contain 0.35% and 0.14%, respectively. Gettens reported zinc for only 6% of the authentic objects he examined and the amounts ranged from 0.02% to 0.07%. The results of some earlier investigations indicate that higher proportions than those reported by Gettens are commonly present when zinc occurs as an accidental component of ancient Chinese copper alloys in general. Chikashige[8] found 0.16%, 0.20%, and 5.00% by a chemical method in three Han mirrors (Table 3), and Sueji Umehara[9] reported 0.38% and 0.44%, also obtained by a chemical method, in two samples from Han vessels. It seems almost certain that zinc is an uncommon minor component of Chinese bronze objects made prior to the Han period.

Magnesium. This element was not detected in the specimens from the mirrors nor in X17b and X61a, but was found by spectrography to be present in the other specimens in amounts ranging from a faint trace to 0.006%. Gettens found 0.001% or less in 79% of the bronzes he examined for this element, and the amounts in the remainder ranged up to 0.007%. The findings of the two investigations are obviously in close agreement for magnesium.

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[7] Gettens, *The Freer Chinese Bronzes*.

[8] Chikashige, "The Composition of Ancient Eastern Bronzes."

[9] Sueji Umehara, "L'analyse chimique des bronzes anciens de la Chine," *Artibus Asiae*, vol. 2 (1927), pp. 247–264.

Calcium. Slight traces of calcium were found by spectrography in five of the specimens and none in the others. Gettens did not find calcium in any of his bronzes. Neither magnesium nor calcium are listed in the tables because they are not really components of the alloys, but are combined with oxygen and silicon in the form of silicates in slag inclusions.

Silicon. This element was found by spectrography to be present in all the specimens. The amounts ranged from 0.004% to 0.021%, the average being 0.009%. Gettens found that the amounts of this element ranged from none to over 1%, the average being about 0.07%. The greater range and higher average of his results may be due in large part to the kind of objects he examined. Large bronze castings in the form of ceremonial vessels may very well contain higher proportions of slag inclusions than smaller cast objects.

Iron. No iron was detected in three of the specimens by spectrography, but amounts ranging from 0.007% to 0.14% were found by this method in nine others, as is shown in Tables 1 and 2. The results of six gravimetric determinations of iron in specimens X201 and X204, which are the basis of the averages for these specimens shown in Table 2, ranged from 0.17% to 0.70%. The iron content of all 14 specimens averaged 0.10%. Gettens found amounts of iron ranging from less than 0.01% to over 1%, the average being about 0.2%. However, not much significance can be attached to these averages because the individual results are so erratically distributed. This erratic variation in the iron content of ancient Chinese alloys is also exhibited by the percentages reported by Chikashige (Table 3).

Nickel. This element was not detected in three of the specimens, but 24 gravimetric determinations of nickel in the others by the accurate dimethylglyoxime method yielded averaged results ranging from 0.05% to 0.33%, as is shown in Tables 1 and 2. The average nickel content of all 14 specimens was 0.11%. Gettens reported percentages of nickel that ranged from none to 0.2%, the average being about 0.03%. Although the ranges of nickel content found in the two investigations are not very different, his average percentage is much lower. Gettens noted that this average is only about twice that of the average percentage of cobalt he found in his bronzes, a ratio considerably lower than that established for the natural occurrence of these two elements. This apparent discrepancy can now be resolved, for it seems evident that his average percentage of nickel is too low. That the nickel content of ancient Chinese copper alloys may sometimes greatly exceed that found in the present investigation is indicated by the percentages reported by Chikashige (Table 3).

Cobalt. No cobalt was found by spectrography in five of the specimens, but amounts ranging from a trace to 0.006% were found in the others by this method, the average for all the specimens being 0.002%. Gettens found amounts ranging from none to 0.1%, and an average of about 0.01%. Although the ranges and averages of the two investigations differ very considerably from each other, the essential fact established by both is that cobalt is a very minor component of ancient Chinese copper alloys.

Arsenic. As is shown in Tables 1 and 2, arsenic was not found by spectrography in two specimens, and amounts ranging from a trace to 0.65% were found by this method in ten others. Two specimens, X201 and X204, were found by gravimetric analysis to contain 1.02% and 0.40% as is shown in Table 2. On the average the specimens contained 0.27% arsenic. Gettens found that 29% of his authentic bronzes contained no arsenic and that the content of the remainder ranged from 0.05% to over 1%, the average being about 0.19%. The findings of the two investigations are in fairly close agreement for arsenic.

Antimony. Only one specimen was found to be free of this element. Eleven were found by spectrography to contain amounts ranging from a trace to 0.12%, as is shown in Tables 1 and 2. Two specimens, X201 and X204, were found by volumetric analysis to contain 0.93% and 5.84% respectively, as is shown in Table 2. If the anomalous amount in X204 is not counted, the average antimony content of the specimens is 0.12%. Gettens found amounts ranging from none to over 1% in his authentic bronzes, the average being 0.12%. Not much significance can be attached to these identical averages because the individual percentages found in both investigations are so erratically distributed. Except for the very high percentage in X204, the findings of the two investigations agree well.

Bismuth. As is shown in Tables 1 and 2 all the specimens were found to contain bismuth. The amounts range from 0.026% to 0.52%, the average being 0.10%. If the isolated high figure of 0.52% is not counted the average is 0.06%. Gettens did not find bismuth in 24% of his authentic bronzes, but found from 0.03% to 0.2% in the others, the average being 0.05%. The results of the two investigations are in satisfactory agreement in respect to bismuth.

Silver. As is shown in Tables 1 and 2 all the specimens were found to contain silver. Those in which none was detected by chemical tests were found by spectrography to contain amounts ranging from 0.001% to 0.008%. The results of twelve individual gravimetric determinations on six specimens ranged from 0.04% to 0.12%, the average being 0.08%. Gettens also found silver in all his objects, but the amounts ranged from 0.01% to 0.3%, the average being 0.13%. The results obtained in this present investigation lie in a distinctly lower range of silver content, but this difference in the findings of the two investigations seems too small to be significant.

Gold. This element was not detected by either chemical tests or spectrography in any of the specimens of the present investigation. Gettens did not find gold in 79% of the authentic objects he examined. He found less than 0.01% in 18%, and 0.01% in the remainder. An investigation of more objects other than ceremonial vessels would probably reveal the presence of similar very small proportions of gold in some.

Sulfur. This element was detected and determined in only two of the specimens, X201 and X204. As is shown in Table 2 the amounts found by gravimetric analysis were 0.42% and 0.26% respectively. Gettens did not search for sulfur in the bronzes he analyzed. Future analyses should include this element, for it may be an indication of the use of sulfide ores.

NON-DESTRUCTIVE X-RAY FLUORESCENCE ANALYSIS OF ANCIENT BRONZE MIRRORS EXCAVATED IN JAPAN

BY MASAAKI SAWADA*

INTRODUCTION

From the tombs in the Yayoi and Tumulus periods of Japan about 2500 bronze mirrors have been excavated. They are classified into two groups: (1) mirrors made in China and brought to Japan, called *hakusai-kyō* (imported Chinese mirrors); (2) imitations of the Chinese mirrors made in Japan, called *bōsei-kyō* (copied Japanese mirrors). The number of the *bōsei-kyō* found so far is double that of the imported Chinese mirrors.[1] These Chinese mirrors are distinguished from the copied Japanese mirrors by comparison of shapes, ornamental patterns and skillfulness of manufacturing technique.

The chemical compositions of the mirrors are also one of the effective measures for distinguishing them. According to published data, imported Chinese mirrors have compositions of 60–75% Cu, 17–30% Sn and 3–7% Pb, while their copied Japanese counterparts have 70–90% Cu, 2–20% Sn and 3–8% Pb.[2] The Japanese varieties tend to have higher Cu and lower Sn content.

One of the mirror types which clearly shows the relationship between the two groups is the so-called *sankakuen shinjū-kyō* (mirrors with a raised-triangle rim, representing figures of fabulous beasts and deities; see fig. 1). These raised-triangle rim mirrors are believed to have been made in the Wei period in China on the basis of age inscriptions on the mirrors, but no mirror of this type has been excavated so far in China.[3] This is one of the archaeologically interesting points much discussed heretofore. It is presumed that the raised-triangle rim mirrors were donated by Chinese kings to the missions sent from Japan in the Yayoi period and these imported mirrors must have been the symbols of political authority at that time in Japan. The number of imported Chinese raised-triangle rim mirrors was not large and the supply became so short that Japanese mirrors were manufactured by copying the Chinese ones.[4] It is therefore archaeologically important to distinguish the imported Chinese mirrors from the Japanese copies.

Up to the present, there have been only a few detailed analytical studies on mirrors, probably because chemical analyses usually require several hundred milligrams of metal. As most of the mirrors are quite corroded on the surfaces, an uncorroded sample from the inside is required. This necessitates the defacement of portions of the mirrors. As a result, the analyses to date have been performed on

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[1] Migaku Tanaka, *Taku-ken-kyo* (On the Archaeological Treasures of Japan, Bronze Bells, Weapons and Mirrors), (Tokyo: Kodansha Ltd., 1977).

[2] Yukio Kobayashi, *Kokyō* (Ancient Mirrors), (Tokyo: Gakushei-Sha Ltd., 1965), p. 48. Yukio Kobayashi. *Kodai no Gijutsu* (On the Ancient Techniques), (Tokyo: Hanawa-Shohō Ltd., 1965). Earle R. Caley, *Analysis of Ancient Metals* (New York: Pergamon Press, 1964), p. 118. Giichi Tanabe, "A Study on the Chemical Compositions of Ancient Bronze Artifacts excavated in Japan," *Journal of the Faculty of Science, University of Tokyo, Sec. V*, vol. 11, part 3 (1962), pp. 281–320.

[3] Kobayashi, *Kokyō*, p. 48.

[4] Tanaka, *Taku-ken-kyō*.

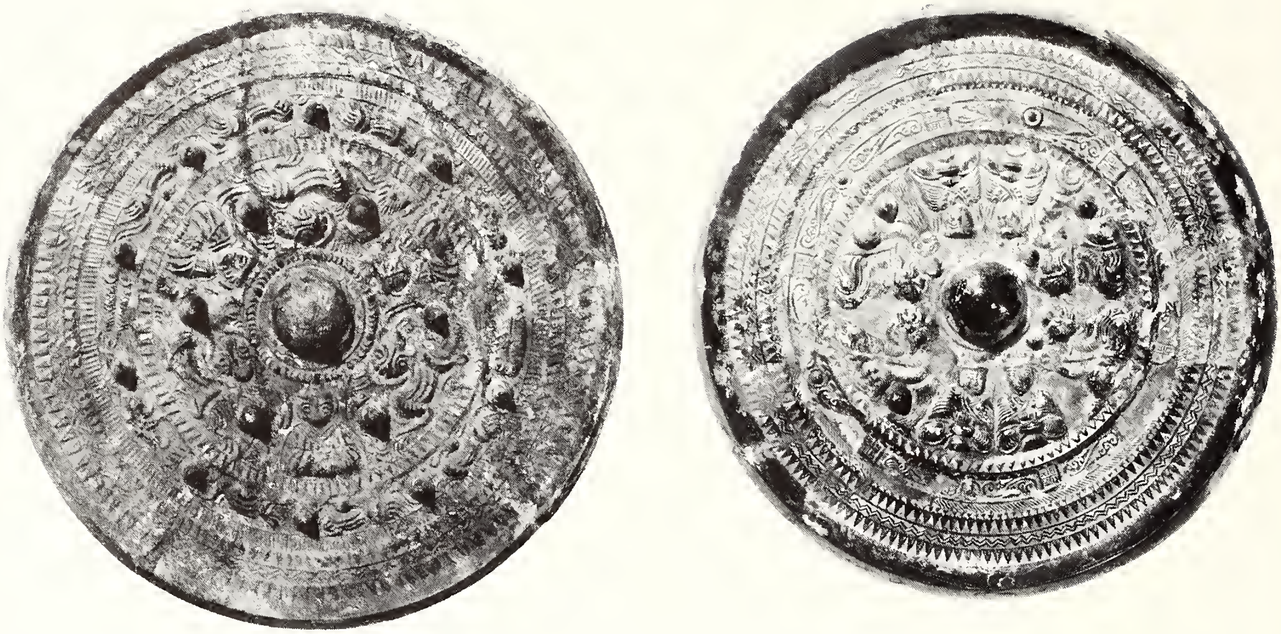

FIG. 1.—Raised-triangle rim mirrors with figures of fabulous beast and deities (left: copied Japanese mirror, right: imported Chinese mirror). About one-third natural size.

fragments unsuitable for archaeological research rather than on complete or intact mirrors.

X-ray fluorescence spectroscopy can be used to analyze the surface of both the complete mirrors and mirror fragments without taking samples. As the mirrors are usually corroded and the outside often differs from the underlying metal, the question arose as to whether Japanese and Chinese mirrors could be chemically differentiated by surface analysis.

EXPERIMENTAL

Mirrors Analyzed

The 79 mirrors selected for this study had been previously identified by archaeologists as *hakusai-kyō* or *bōsei-kyō*. The mirrors selected were those which could be clearly differentiated on the basis of visual characteristics. Forty-two mirrors identified as imported Chinese examples and thirty-seven identified as copied Japanese mirrors were used as the basis for the work reported here. Most of the mirrors studied were drawn from the collection of the Kyoto University Faculty of Archaeology. Of these, 27 Chinese mirrors and 20 Japanese mirrors are in the collection of Kyoto University; the rest are from prefectural collections.

Analytical Method

An X-ray fluorescence spectrometer of the Rigaku-Denki Company was used with the following conditions:

Voltage: 40 kVp
Current: 20 mA

Full Scale: $1 \times 10^3 - 2 \times 10^4$ counts
Time Constant: 2 sec.
Scanning Speed: 1°/min.
Crystal: LiF
Target: Cr
Detector: scintillation counter

The irradiation area of this instrument for a sample is usually 30 mm in diameter: in the present case the area was reduced to 15 mm in diameter by masking the mirror with aluminum sheet with a circular window.

Using this arrangement the major bronze elements, copper (Cu), tin (Sn) and lead (Pb), were detected as well as such minor constituents as arsenic (As), bismuth (Bi), silver (Ag), iron (Fe) and antimony (Sb).

For the analytical comparison, the ratios of tin to lead on the surfaces of the mirrors were determined by measuring the intensity ratios of the X-ray lines, PbLγ/CuKβ and SnKα/CuKβ, thus using Cu as an internal reference standard.

RESULTS AND DISCUSSION

The results for the 79 mirrors analyzed are shown in Table III. Each mirror was analyzed in a number of surface locations. In the table, the type of surface at the spot analyzed is shown along with the PbLγ/CuKβ and SnKα/CuKβ count ratios, which we refer to below as (x, y) for convenience. Mirror type, archaeological provenance, and some statistics of each analysis are also shown.

Initially, one mirror was selected from each group; various parts of each mirror were analyzed, with all corrosion included. The results of analysis for mirror no. 4 (Chinese) and no. 52 (Japanese) are plotted in Figure 2. The structure of the data appears to be quite linear, with the (x, y) pairs falling along lines of constant proportion.

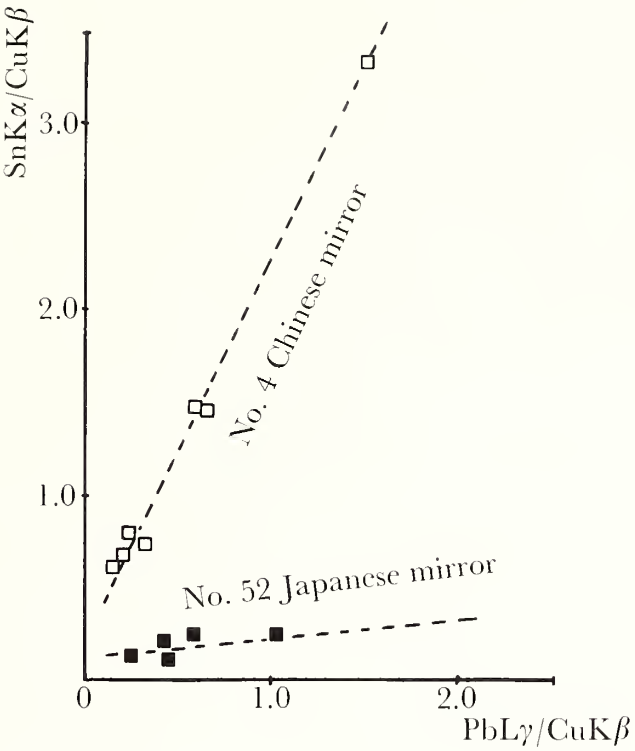

FIG. 2.—The distribution of analytical data in various parts of the same sample.

Assuming for the moment that the data are linear, a linear regression analysis can be performed, using the PbLγ/CuKβ and SnKα/CuKβ ratios as x and y. The slope of the line thus determined can be seen to be equal to

$$\frac{\mathrm{SnK}\alpha/\mathrm{CuK}\beta}{\mathrm{PbL}\gamma/\mathrm{CuK}\beta}, \quad \text{or to} \quad \mathrm{SnK}\alpha/\mathrm{PbL}\gamma.$$

Since the tin concentration should be proportional to the SnKα counts (and similarly for lead), we have:

$$\text{Slope} = k\,\frac{\text{Sn\%}}{\text{Pb\%}}$$

It can also be reasoned that the line should probably intercept the y-axis at the origin;

if the spectrometer is allowed to run half the time, half of the counts will be accumulated in both the SnKα and PbLγ channels. If the time of a run is reduced, the counts will tend towards (0,0) as a limit; similar arguments can be applied to attenuation of X-rays by unfavorable geometry.

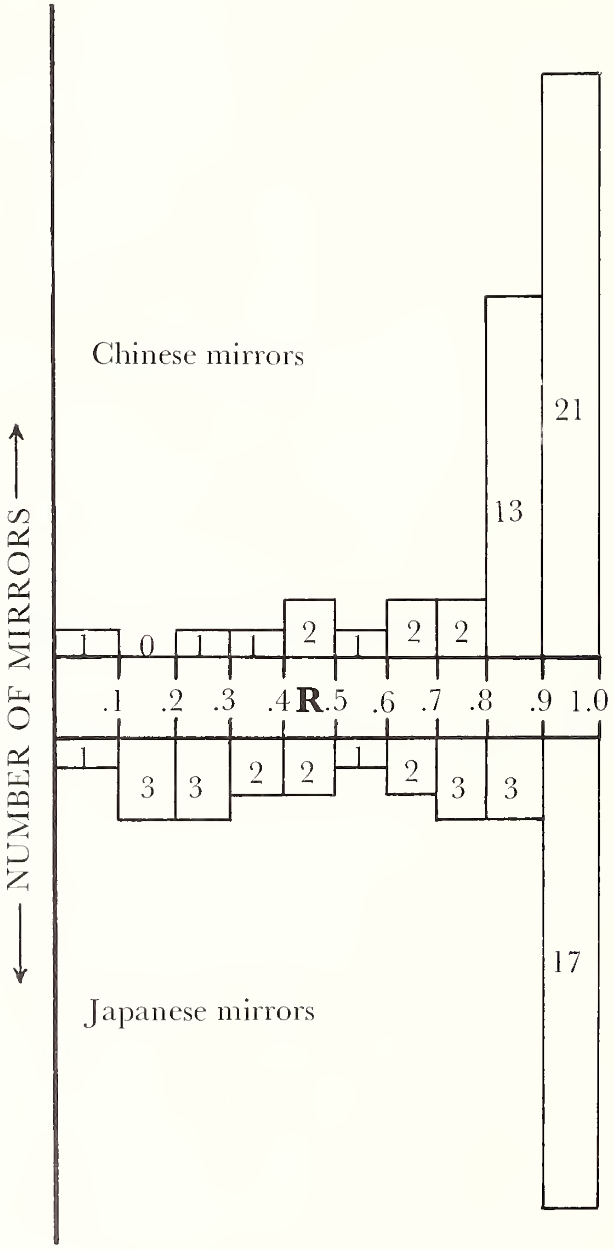

FIG. 3.—Histograms showing correlation coefficients (R) in both groups of mirrors.

A standard least-squares linear regression analysis was performed on each set of (x, y) data, and slopes and intercepts determined. To test the linearity of the data, correlation coefficients were also determined. These are listed in Table III and shown as histograms in Figure 3. It can be clearly seen that the majority of correlation coefficients lie between 0.8 and 1.0; a good indication of the linearity of the data.

After the least squares linear regression had been performed, the slope of the function through the origin was also determined by the following equation:[5]

$$\text{Slope to intercept } (0,0) = \frac{\sum_{i=1}^{n} (x_i y_i)}{\sum_{i=1}^{n} (x_i)^2}$$

$$= \text{adjusted slope}$$

It can be shown that the use of adjusted slope in the analyses below reduces the scatter of the slope data and makes the distribution of slopes approach more clearly to the normal distribution.

To answer the question of the relationship of the X-ray surface analysis data to the actual composition of the mirrors, we have compared the X-ray results to those derived from analysis by wet chemistry for 6 mirrors in Table I. The slope bears a clear relation to the Sn/Pb ratio. In Table Ib, the results from Table Ia are ranked by magnitude, starting with the greatest. Ranking of the least-squares slope and of the adjusted slope from the X-ray results is identical, and agrees very closely

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[5] John Mandel, *The Statistical Analysis of Experimental Data* (New York: John Wiley & Sons, Inc., 1964), 245 pp.

TABLE I

Wet Analysis vs. X-ray Spectrometry

a. Amounts

		Wet Analysis					X-ray spectrometry				
Mirror	Origin	Cu	Sn	Pb	Total	Sn/Pb	$\bar{x}$	$\bar{y}$	Intercept	Slope	Adjusted slope
1	Chinese	74.5	17.8	3.4	95.7	5.24	0.27	0.72	0.16	2.10	2.59
29	Chinese	66.7	20.6	7.0	94.3	2.94	0.60	1.04	0.43	1.01	1.58
39	Chinese	74.5	14.5	5.7	94.7	2.54	0.61	0.56	0.05	0.84	0.90
40	Chinese	74.4	17.8	5.6	97.8	3.18	0.38	1.22	0.20	1.22	1.59
41	Chinese	77.0	17.9	3.4	98.3	5.26	0.42	0.91	0.15	1.80	2.09
43	Japanese	78.3	13.6	9.1	101.0	1.50	0.82	0.46	0.26	0.24	0.52

b. Ranks

Mirror	Cu/Sn	Cu/Pb	Sn/Pb	Intercept	Slope	Adjusted slope
1	4	2	2	4	1	1
29	6	5	4	1	4	4
39	2	4	5	6	5	5
40	5	3	3	3	3	3
41	3	1	1	5	2	2
43	1	6	6	2	6	6

with the ranking of Sn/Pb ratios from wet chemical analysis. The only discrepancy in the latter agreement is that mirrors 1 and 41 are interchanged. These mirrors differ very little in Sn/Pb ratio, and an interchanging of these ranks does not seem significant.

It should, therefore, be possible to determine the Sn/Pb ratios from our surface analyses. The least-squares linear regression lines for slope versus Sn/Pb ratio and adjusted slope versus Sn/Pb ratio can be seen in Figure 4. The equations of these lines can be used to determine the Sn/Pb ratios in mirrors from the slopes calculated from surface analysis data.

The questions of errors and confidence limits in this statistical analysis are quite complex, and will not be taken up here. It seems, *a priori*, that the higher the correlation coefficient (R) of the (x, y) values for a given mirror, the more well-defined is the slope, and the better the estimate of the ratio of concentrations, Sn/Pb, will tend to be. It may be that analyses with $R < 0.85$ should be disregarded, or that a sufficient number of analyses should be made on any mirror so that $R > 0.90$. With the idea of improving the correlation of the (x, y) points, 10 mirrors were subjected to statistical analysis on the basis of "clean" readings only (marked C in Table III) or with apparent outlying observations omitted (marked "without analysis No. 5," or otherwise, in Table III). This sort of data selection did not significantly affect the errors in distinguishing Chinese mirrors from Japanese copies.

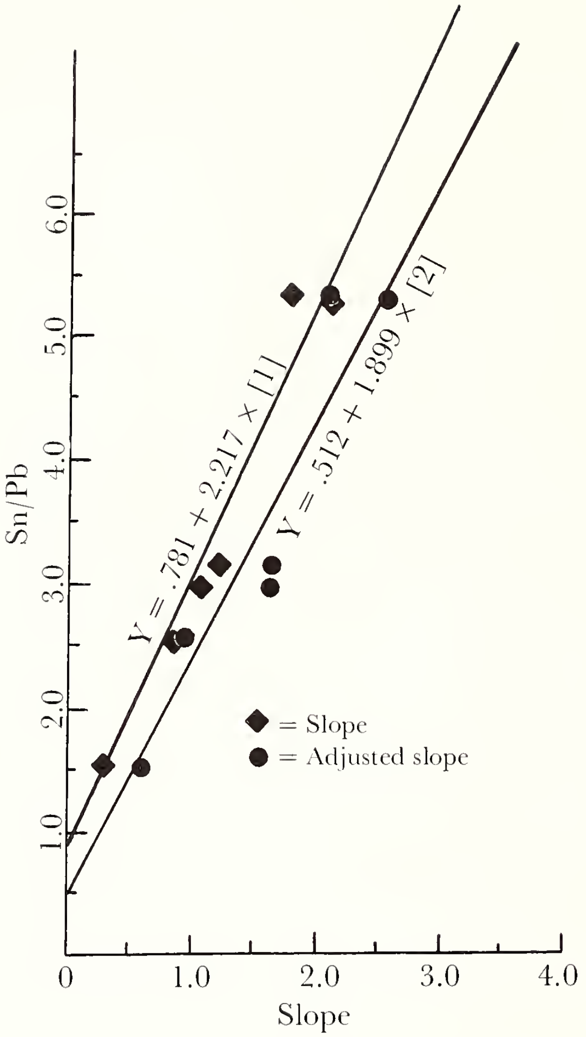

FIG. 4.—Sn/Pb ratio determined by wet chemistry versus the slopes from our X-ray fluorescence data. [1] is the least squares linear regression equation for the line fitted to data using the original slopes, [2] using adjusted slopes.

The variations in our determinations of the Sn/Pb ratio of the mirrors stem from at least four factors:

(a) The variation of composition between individual mirrors of the two classes.

(b) The variation of composition within any one mirror.

(c) Variable removal or displacement of the original elements in the metal by corrosion, later cleaning, etc.

(d) Errors in measurement of the X-ray fluorescence data.

Of these, only the first can be assessed at the moment, though corrosion will be dealt with briefly below. If we look at Tanabe's data[6] (fig. 5), we can clearly see the variation that he found between mirrors of the Japanese and Chinese classes. In Table II the ranges of Sn/Pb ratios found by Tanabe are shown in the first row, followed by the slopes derived from those ratios by equation (1) in Figure 4. It can be seen that the ranges do overlap, especially between the Chinese and Japanese mirrors of the Tumulus period. The ranges agree well between Tanabe's data and our data, and a similar region of overlap can be seen.

If the adjusted slopes from our analyses are plotted, we get the histogram shown in Figure 6. In a slope range below 0.3, only Japanese mirrors are found; above 1.7, only Chinese mirrors, with one exception; in the intermediate range, the area from 0.3 to 0.7 contains mostly Japanese mirrors (16 Japanese and 1 Chinese), and it is most probable that, if the slope falls in this range, the mirror may be identified as Japanese. The area from slope 1.1 to slope 1.7 contains predominantly Chinese mirrors (20 Chinese and 6 Japanese) and mirrors with slopes in this range will probably be Chinese. Mirrors with slopes from 0.7 to 1.1, determined by our method,

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[6] Tanabe, "... Chemical Compositions ...", p. 278; see also W. T. Chase and T. O. Ziebold, "Ternary Representations of Ancient Chinese Bronze Compositions," in *Archaeological Chemistry* II, ed. Giles Carter, American Chemical Society Advances in Chemistry Series No. 171 (Washington, D.C., in press).

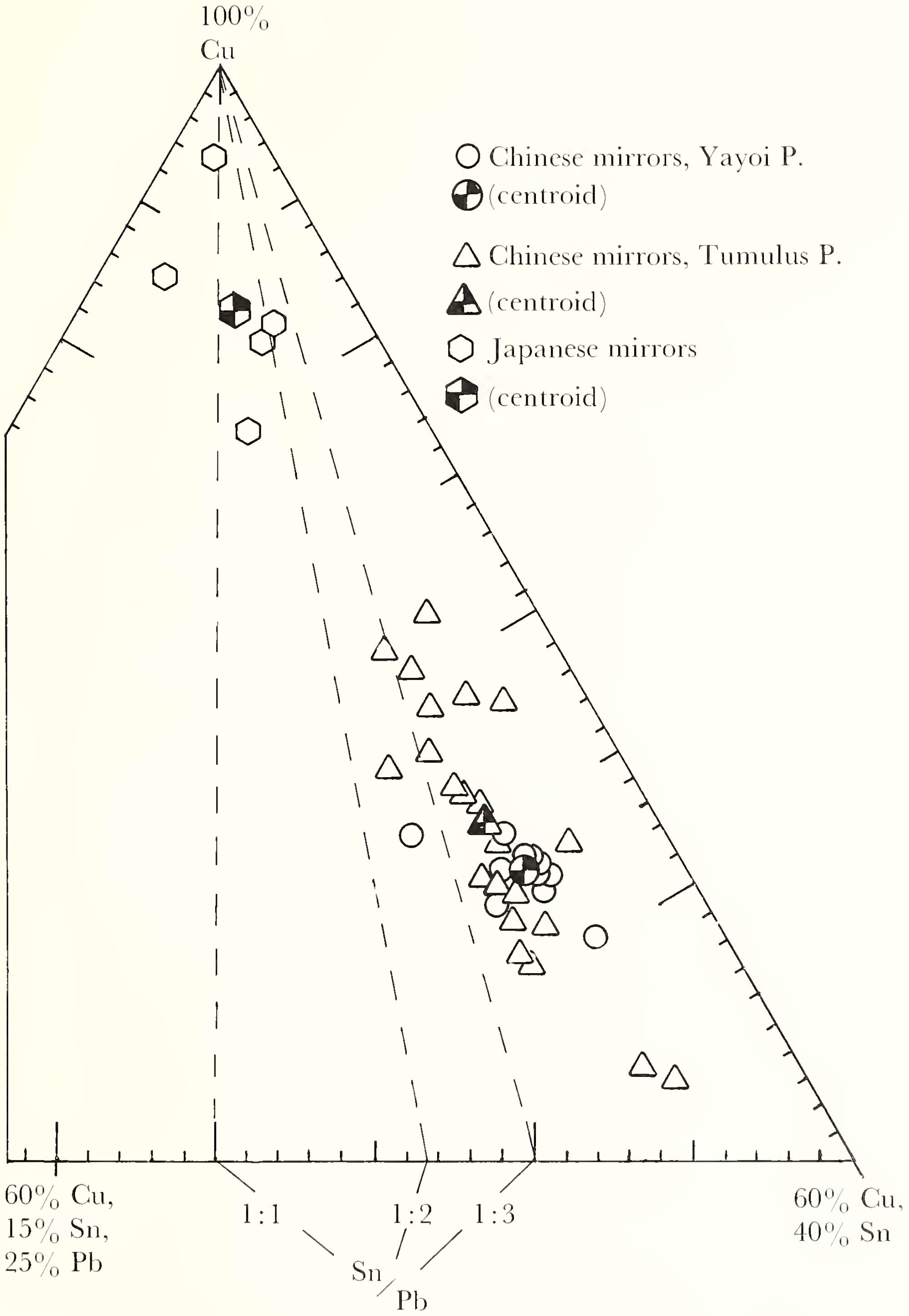


Fig. 5.—Detail of ternary plot (Cu-Sn-Pb)of mirror analyses by Tanabe, showing groups by composition. Lines of constant Sn/Pb ratio are also shown.

TABLE II

Slopes determined from Tanabe's data compared with slopes from our data

		Chinese mirrors		Japanese mirrors
		Yayoi period*	Tumulus period*	Tumulus period*
Data from Tanabe[†]	Sn/Pb	6.77–3.87	7.74–2.36 (131)[§]	2.91–0.42
	Slope[‡]	2.70–1.40	3.14–0.71 (.24)	0.96–0.16
Our data	Slope	2.74– –0.80		2.23– –0.92
	Adjusted slope	2.12–0.33		2.51– –0.08

* Periodization only applies to Tanabe's data here.

[†] See Footnote 2.

[‡] From equation 1, Figure 4.

[§] One apparent outlier has this value.

have an equal probability of being Chinese or Japanese, 7 Chinese and 7 Japanese falling in this area. Again, the overlap of adjusted slopes seen in Table II agrees in magnitude with these findings.

Thus, if a mirror was determined by X-ray fluorescence to have a slope of the

$$\frac{\mathrm{SnK}\alpha/\mathrm{CuK}\beta}{\mathrm{PbL}\gamma/\mathrm{CuK}\beta}$$

line of greater than 1.1, we could label it as probably Chinese; if the slope was less than 0.7, it could be labelled probably Japanese; mirrors with intermediate slope would have to be labelled not clearly differentiated.

So, we can quite reliably classify about 80% of the mirrors with this method. Since the mean of the distribution of the (x, y) points for each mirror will lie along the line

$$y = 0.0 + (\text{adjusted slope})x.$$

the differentiation can also be made on a graph like that shown in Figure 7.

The condition and distribution of the corrosion products on the surface also determine the analytical data, but in a very complex way. Figures 8a and 8b show all analytical data for Chinese and Japanese mirrors in this study, with the points labelled in terms of the kind of patina. The results vary according to the surface conditions; corrosion-free areas tend to have low Sn/Cu and Pb/Cu ratios, while the blue and green areas tend towards higher values. The reasons for the variability in the data on corroded surfaces depend on the corrosion mechanics and environment present, and must be left for later analysis. We cannot, at this time, propose any theoretical or mathematical model to account for these effects.

SUMMARY

Thus, a distinction between Chinese and Japanese mirrors of this period seems to be possible, in a majority of cases, by determining the tin to lead ratios non-destructively without taking corrosion conditions of the

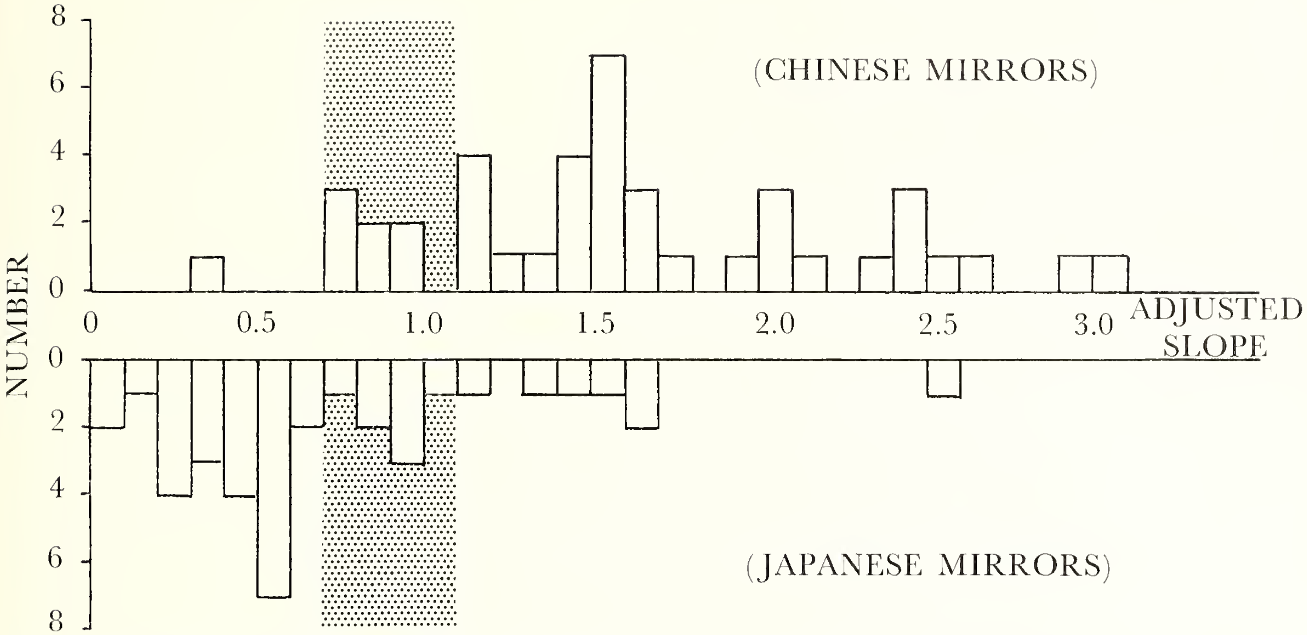


FIG. 6.—Histogram of adjusted slopes from analysis versus number of Chinese and Japanese mirrors. The areas of the two differentiated groups and the area of uncertainty are also shown.

surfaces into account. Obviously this is not a perfect method of distinguishing the two groups, but it can be helpful to archaeologists, who depend mostly on typological study to distinguish such mirrors.

In the future, more data will be available from non-destructive X-ray fluorescence analysis; it will certainly contribute to the archaeology of bronze mirrors excavated in Japan.

With further investigation into the relationship of chemical composition to surface analysis by X-ray spectrometry, there may be a possibility of finding the true chemical composition by analyzing mirrors in any condition, even corroded areas.

ACKNOWLEDGEMENTS

This study is a part of the program of 'The Fundamental Study on the Non-destructive Analysis of Metal Objects', which has been headed by Professor Takayasu Higuchi, Kyoto University. The present author wishes to thank Prof. T. Higuchi.

Part of the expense was met by a grant-in-aid for Scientific Research of the Ministry of Education to which the author's thanks are due. The author is indebted to Mr. Y. Emoto and Dr. H. Mabuchi of Tokyo National Cultural Properties Research Institute, and to the investigating staff for this study, Mr. M. Sahara, Mr. T. Yamamoto and Mr. T. Akiyama of Nara National Cultural Properties Research Institute, for their helpful discussions and suggestions. Finally, the author's thanks go to Mr. W. T. Chase of the Freer Gallery of Art for help with the revision of this paper.

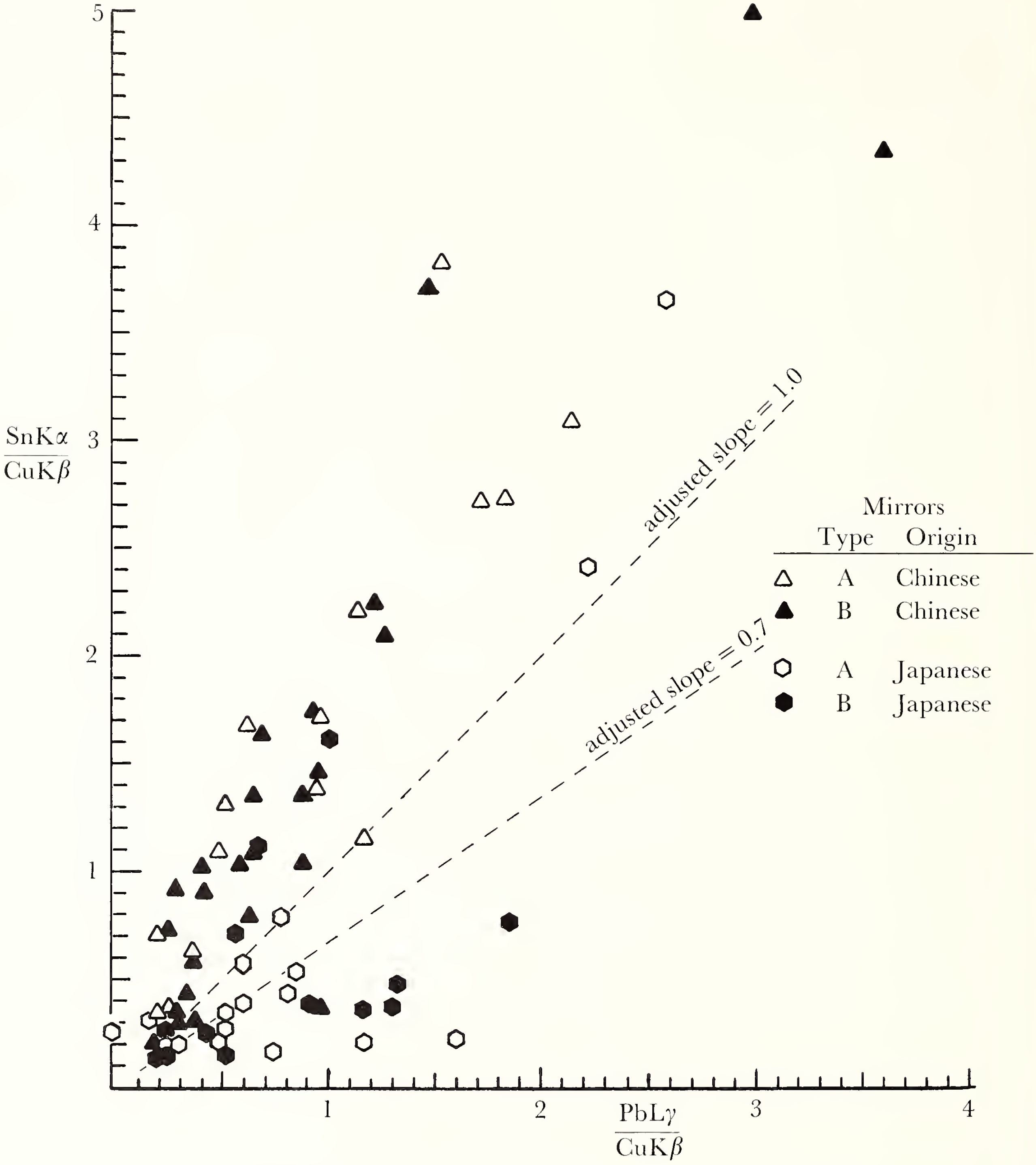
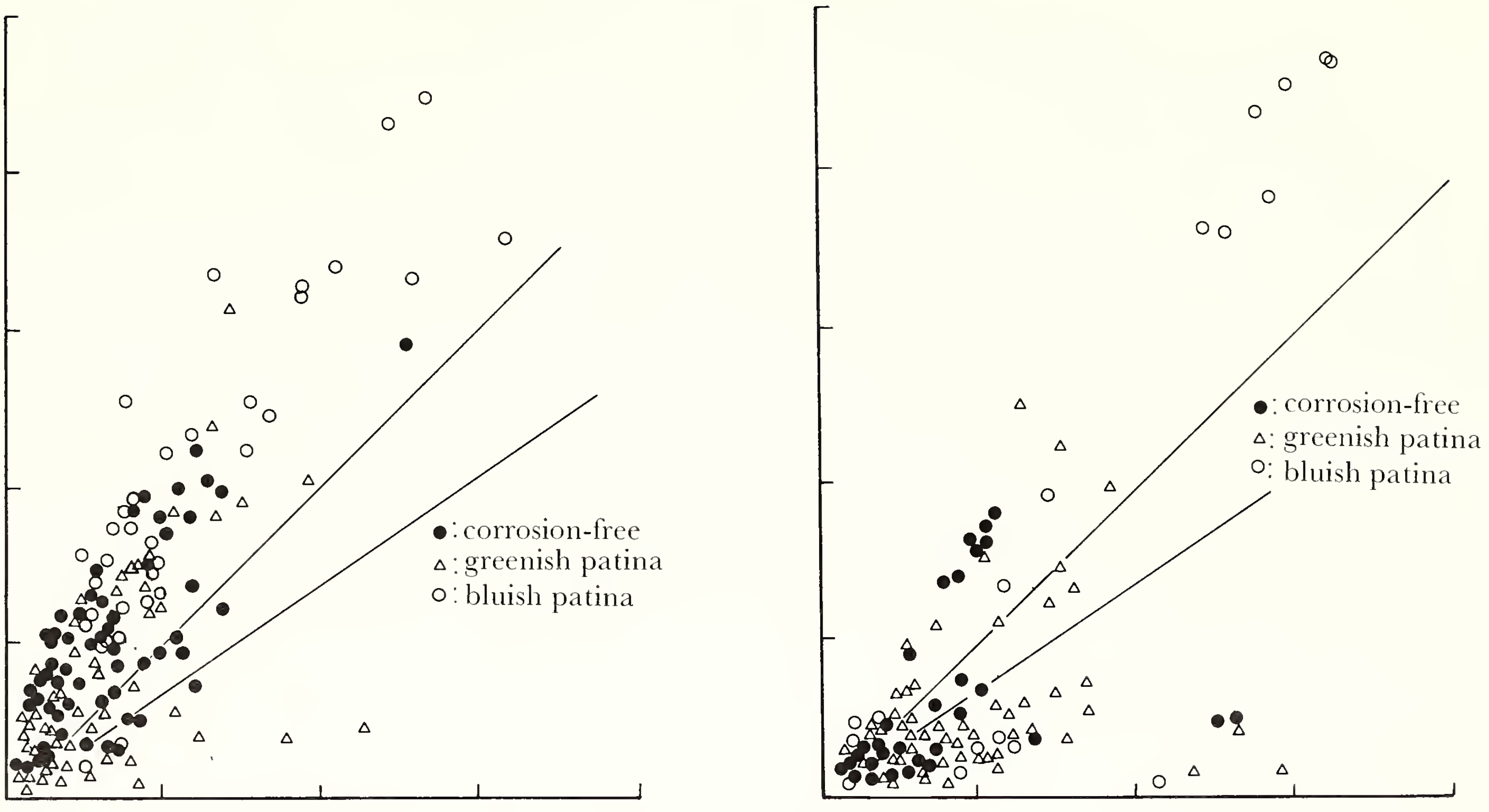


Fig. 7.—PbLγ/CuKβ and SnKα/CuKβ ratios of 79 Chinese and Japanese mirrors; the centroid of each distribution (x,y) is plotted. The two dotted lines show the area of uncertainty, and are repeated on Figure 8.



a.

b.

FIG. 8.—PbLγ/CuKβ and SnKα/CuKβ ratios as determined on the three types of surfaces on the mirrors. Figure 8a shows Chinese mirrors, and 8b shows Japanese mirrors.

TABLE III

Surface analysis by X-ray fluorescence of Chinese and Japanese mirrors

Mirror Number[*]	Type[†]	Archaeological Provenance	Analysis Number	Surface Condition[‡]	SnKα/CuKβ	PbLγ/CuKβ
1	B	Hyōgo Prefecture	1	C	0.68	0.20
		N=11 R=0.966[§]	2	G	1.03	0.44
		X MEAN=0.265 Y MEAN=0.717	3	C	1.43	0.60
		Y =0.162+2.098X	4	G	0.57	0.18
		ADJUSTED SLOPE=2.585	5	G	0.85	0.31
			6	G	0.44	0.15
			7	G	0.79	0.24
			8	G	0.52	0.16
			9	G	0.68	0.24
			10	G	0.35	0.14
			11	G	0.55	0.25
2	A	Kumamoto Prefecture	1	G	0.23	0.29
		N=5 R=−0.203	2	G	0.23	0.31
		X MEAN=0.276 Y MEAN=0.312	3	G	0.35	0.28
		Y=0.436+−0.449X	4	G	0.32	0.21
		ADJUSTED SLOPE=1.106	5	G	0.43	0.29
3	B	Kyōto Prefecture	1	G	2.38	1.31
		N=4 R=0.965	2	G	1.55	0.91
		X MEAN=0.938 Y MEAN=1.730	3	G	1.84	1.08
		Y=0.443+1.372X	4	G	1.15	0.45
		ADJUSTED SLOPE=1.797				
4	A	Kyōto Prefecture	1	C	1.45	0.62
		N=7 R=0.996	2	C	1.46	0.60
		X MEAN=0.519 Y MEAN=1.293	3	C	0.62	0.15
		Y=0.233+2.044X	4	C	0.67	0.20
		ADJUSTED SLOPE=2.306	5	C	0.79	0.24
			6	C	3.33	1.50
			7	C	0.73	0.32
5	B	Kyōto Prefecture	1	G	1.92	0.87
		N=4 R=0.988	2	G	1.18	0.54
		X MEAN=0.660 Y MEAN=1.363	3	B	1.85	0.85
		Y=−0.442+2.735X	4	G	0.50	0.38
		ADJUSTED SLOPE=2.125				
6	B	Kyōto Prefecture	1	C	1.04	0.30
		N=4 R=0.405	2	C	1.19	0.35
		X MEAN=0.302 Y MEAN=0.908	3	C	0.69	0.19
		Y=0.531+1.244X	4	G	0.71	0.37
		ADJUSTED SLOPE=2.907				
7	A	Kyōto Prefecture	1	B	2.52	0.76
		N=4 R=0.993	2		3.34	1.32
		X MEAN=1.538 Y MEAN=3.830	3	G	3.71	1.57
		Y=0.939+1.880X	4		5.75	2.50
		ADJUSTED SLOPE=2.404				
8	A	Kyōto Prefecture	1	C	1.05	0.26
		N=4 R=0.982	2	C	1.02	0.28
		X MEAN=0.822 Y MEAN=2.078	3	C	1.39	0.75
		Y=0.243+2.230X	4	G	4.85	2.00
		ADJUSTED SLOPE=2.400				
9	A	Kyōto Prefecture	1	B	2.45	1.68
		N=4 R=0.885	2	B	2.53	1.55
		X MEAN=1.842 Y MEAN=2.745	3		4.29	2.43
		Y=−1.741+2.435X	4	B	1.71	1.71
		ADJUSTED SLOPE=1.522				
10	A	Kyōto Prefecture	1	C	0.77	0.23
		N=4 R=0.738	2	G	1.27	0.47
		X MEAN=0.488 Y MEAN=1.088	3	G	1.13	0.50
		Y=0.716+0.762X	4	B	1.18	0.75
		ADJUSTED SLOPE=2.048				
11	A	Kyōto Prefecture	1	G	0.68	0.32
		N=4 R=0.959	2	B	1.19	0.46
		X MEAN=1.142 Y MEAN=2.220	3	B	2.22	1.53
		Y=0.043+1.905X	4	G	4.79	2.26
		ADJUSTED SLOPE=1.931				
12	A	Kyōto Prefecture	1	B	1.08	0.50
		N=4 R=0.935	2	B	4.46	2.68
		X MEAN=1.728 Y MEAN=2.732	3	B	2.13	1.84
		Y=0.133+1.505X	4	B	3.26	1.89
		ADJUSTED SLOPE=1.569				
13	A	Kyōto Prefecture	1	C	0.85	0.27
		N=4 R=0.986	2	C	0.75	0.20
		X MEAN=0.958 Y MEAN=1.728	3	B	1.98	0.77
		Y=0.728+1.044X	4	B	3.33	2.59
		ADJUSTED SLOPE=1.420				
14	A	Ōsaka Prefecture	1	C	0.29	0.25
		N=5 R=−0.272	2	G	0.34	0.24
		X MEAN=0.218 Y MEAN=0.310	3	G	0.45	0.18
		Y=0.484+−0.799X	4	G	0.21	0.19
		ADJUSTED SLOPE=1.384	5	C	0.26	0.23
15	A	Kyōto Prefecture	1	C	1.96	1.38
		N=5 R=0.960	2	C	1.79	1.17
		X MEAN=0.952 Y MEAN=1.386	3	C	1.05	0.84
		Y=0.040+1.414X	4	C	1.18	0.70
		ADJUSTED SLOPE=1.453	5	C	0.95	0.67

[*] Mirrors 1 to 42: Chinese
43 to 79: Japanese

[†] Type A: Triangle-rim mirrors
Type B: Others

[‡] Surface conditions: C = clean metal
G = greenish patina
B = bluish patina

[§] N = Number of (x,y) observations
R = Correlation coefficient

The means of the x and y distributions ($\bar{x}, \bar{y}$) are shown below, as is the regression equation derived by least squares and the "adjusted" slope—see text.

TABLE III (continued)

Mirror Number[*]	Type[†]	Archaeological Provenance	Analysis Number	Surface Condition[‡]	SnKα / CuKβ	PbLγ / CuKβ
16	A	Kyōto Prefecture	1	B	3.61	2.43
		N=10 R=0.989	2	B	1.91	1.43
		X MEAN=2.139 Y MEAN=3.102	3	G	0.92	0.53
		Y=0.025+1.439X	4	B	4.34	2.77
		ADJUSTED SLOPE=1.449	5	B	4.66	3.23
			6	B	4.51	2.98
			7	B	2.20	1.53
			8	G	1.50	1.04
			9	B	3.79	2.87
			10	B	3.58	2.58
17	A	Kyōto Prefecture	1	G	1.97	0.76
		N=7 R=0.669	2	G	1.35	0.51
		X MEAN=0.621 Y MEAN=1.667	3	G	1.72	0.83
		Y=0.605+1.701X	4	G	1.06	0.46
		ADJUSTED SLOPE=2.642	5	B	2.06	0.64
			6	B	1.83	0.64
			7	G	1.68	0.51
18	B	Kyōto University	1	G	0.22	0.27
		N=13 R=0.761	2	G	0.96	0.83
		X MEAN=0.563 Y MEAN=0.398	3	G	0.25	0.80
		Y=0.007+0.718X	4	G	0.25	0.25
		ADJUSTED SLOPE=0.709	5	G	0.46	0.57
			6	G	0.12	0.18
			7	G	1.02	1.14
			8	G	0.21	0.28
			9	G	0.22	0.29
			10	G	0.31	0.80
			11	G	0.47	0.56
			12	G	0.25	0.51
			13	G	0.43	0.84
19	B	Kyōto University	1	G	0.06	0.15
		N=16 R=0.636	2	B	0.06	0.15
		X MEAN=0.226 Y MEAN=0.185	3	B	0.12	0.27
		Y=0.019+0.733X	4	B	0.31	0.26
		ADJUSTED SLOPE=0.805	5	G	0.11	0.16
			6	B	0.42	0.17
			7	G	0.27	0.27
			8	G	0.12	0.20
			9	G	0.39	0.58
			10	C	0.27	0.24
			11	G	0.10	0.19
			12	G	0.04	0.14
			13	G	0.28	0.27
			14	C	0.14	0.17
			15	C	0.05	0.13
			16	G	0.22	0.26
20	B	Kyōto University	1	G	0.07	0.39
		N=18 R=0.477	2	G	0.22	0.44
		X MEAN=0.391 Y MEAN=0.298	3	G	0.17	0.55
		Y=0.076+0.568X	4	G	0.21	0.63
		ADJUSTED SLOPE=0.716	5	G	0.07	0.44
			6	G	0.07	0.24
			7	G	0.07	0.22
			8	G	0.56	0.47
			9	G	0.28	0.72
			10	G	0.25	0.64
			11	C	1.18	0.89
			12	C	0.61	0.32
			13	C	0.30	0.19
			14	C	0.27	0.14
			15	C	0.24	0.20
			16	C	0.26	0.14
			17	C	0.25	0.16
			18	C	0.28	0.26
21	B	Kyōto University	1	C	0.25	0.70
		N=15 R=0.475	2	C	0.24	0.62
		X MEAN=0.971 Y MEAN=0.361	3	G	0.46	2.27
		Y.=0.225+0.140X	4	C	0.26	0.75
		ADJUSTED SLOPE=0.329	5	C	0.25	0.70
		"C" Data Only:	6	G	0.38	1.82
		N=11 R=0.952	7	C	0.25	0.68
		X MEAN=0.767 Y MEAN=0.351	8	C	0.26	0.68
		Y=−0.340+0.902X	9	B	0.30	0.79
		ADJUSTED SLOPE=0.478	10	G	0.41	1.24
			11	C	0.26	0.63
			12	C	0.35	0.74
			13	C	0.50	0.88
			14	C	0.74	1.23
			15	C	0.51	0.83
22	B	Kyōto University	1	B	1.51	0.98
		N=12 R=0.980	2	B	1.03	0.67
		X MEAN=0.948 Y MEAN=1.453	3	B	1.20	0.81
		Y=−0.063+1.600X	4	B	1.21	0.76
		ADJUSTED SLOPE=1.542	5	B	1.32	1.07
			6	B	1.04	0.64
			7	B	1.25	0.90
			8	B	0.98	0.66
			9	B	1.44	0.96
			10	B	3.41	2.13
			11	B	1.64	0.95
			12	B	1.41	0.85
23	B	Kyōto University	1	C	0.27	0.22
		N=16 R=−0.022	2	C	0.30	0.27
		X MEAN=0.313 Y MEAN=0.304	3	C	0.29	0.29
		Y=0.311+−0.022X	4	G	0.14	0.29
		ADJUSTED SLOPE=0.754	5	G	0.16	0.17
		"C" Data Only:	6	G	0.10	0.88
		N=6 R=0.413	7	G	0.20	0.22
		X MEAN=0.302 Y MEAN=0.360	8	G	0.19	0.17
		Y=0.075+0.966X	9	G	0.22	0.25
		ADJUSTED SLOPE=1.206	10	G	0.16	0.17
			11	G	0.60	0.28
			12	C	0.67	0.32
			13	B	0.46	0.45
			14	C	0.40	0.42
			15	C	0.27	0.29
			16	G	0.44	0.32

Table III (continued)

Mirror Number*	Type†	Archaeological Provenance	Analysis Number	Surface Condition‡	$\frac{SnK\alpha}{CuK\beta}$	$\frac{PbL\gamma}{CuK\beta}$
24	B	Kyōto University	1	C	1.74	1.09
		N=12 R=0.784	2	C	1.71	0.94
		X MEAN=0.893 Y MEAN=1.370	3	C	2.08	1.30
		Y=0.126+1.394X	4	C	2.23	1.22
		ADJUSTED SLOPE=1.521	5	C	1.78	0.83
			6	G	0.40	0.19
			7	G	0.91	0.47
			8	G	1.48	0.87
			9	C	0.68	0.73
			10	G	1.35	1.20
			11	G	0.91	1.00
			12	G	1.19	0.88
25	B	Kyōto University	1	B	1.16	0.52
		N=15 R=0.841	2	B	2.19	1.02
		X MEAN=1.227 Y MEAN=2.271	3	B	1.51	0.66
		Y=1.282+0.807X	4	B	1.79	0.79
		ADJUSTED SLOPE=1.579	5	B	1.66	0.82
			6	B	3.42	3.52
			7	B	1.59	0.55
			8	B	1.70	0.72
			9	B	2.38	1.20
			10	B	1.86	0.86
			11	B	2.66	1.41
			12	G	3.16	1.43
			13	B	3.15	1.85
			14	B	2.73	1.46
			15	B	3.11	1.59
26	B	Kyōto Prefecture	1	B	1.10	0.79
		N=15 R=0.881	2	C	0.71	0.44
		X MEAN=0.889 Y MEAN=1.053	3	C	0.79	0.40
		Y=0.180+0.981X	4	G	0.33	0.42
		ADJUSTED SLOPE=1.115	5	G	0.37	0.34
			6	G	0.29	0.36
			7	B	0.95	0.55
			8	G	0.53	0.42
			9	B	1.16	0.50
			10	G	2.05	1.98
			11	G	0.55	1.08
			12	C	0.92	0.96
			13	C	1.19	1.42
			14	G	2.90	2.56
			15	C	1.95	1.12
27	B	Siga Prefecture	1	C	0.85	0.50
		N=14 R=0.900	2	B	1.25	0.67
		X MEAN=0.647 Y MEAN=1.103	3	B	1.19	0.53
		Y=0.154+1.466X	4	B	1.77	1.09
		ADJUSTED SLOPE=1.679	5	G	0.74	0.38
			6	C	1.03	0.55
			7	C	1.47	0.82
			8	C	0.88	0.40
			9	C	0.95	0.81
			10	C	1.25	0.75
			11	C	0.79	0.54
			12	G	0.62	0.41
			13	C	1.82	1.06
			14	G	0.83	0.55
28	B	Siga Prefecture	1	C	0.82	0.55
		N=16 R=0.871	2	C	0.91	0.65
		X MEAN=0.639 Y MEAN=0.814	3	G	1.75	1.27
		Y=0.098+1.121X	4	C	0.83	0.66
		ADJUSTED SLOPE=1.256	5	G	0.47	0.35
			6	G	0.49	0.29
			7	G	0.79	0.93
			8	G	0.55	0.34
			9	C	0.84	0.72
			10	G	0.65	0.69
			11	G	0.53	0.35
			12	G	0.55	0.65
			13	C	0.71	0.53
			14	C	1.07	0.73
			15	C	0.92	0.67
			16	G	1.15	0.84
29	B	Hyōgo Prefecture	1	G	1.28	0.64
		N=10 R=0.808	2	B	1.36	0.59
		X MEAN=0.601 Y MEAN=1.040	3	C	1.05	0.40
		Y=0.432+1.012X	4	G	1.89	1.51
		ADJUSTED SLOPE=1.577	5	C	1.10	0.53
			6	G	0.97	0.57
			7	G	0.63	0.35
			8	G	0.49	0.48
			9	G	0.61	0.48
			10	C	1.02	0.46
30	A	Gitu Prefecture	1	C	1.48	1.26
		N=15 R=0.810	2	C	1.50	2.33
		X MEAN=1.181 Y MEAN=1.176	3	C	1.69	1.27
		Y=0.592+0.494X	4	B	1.42	1.50
		ADJUSTED SLOPE=0.912	5	G	1.43	2.01
			6	G	1.08	0.86
			7	G	0.81	0.92
			8	G	0.96	0.83
			9	G	1.47	1.51
			10	C	1.08	1.21
			11	G	1.21	1.40
			12	G	0.95	0.70
			13	C	0.62	0.42
			14	C	1.33	1.23
			15	C	0.61	0.26
31	B	Saga Prefecture	1	G	5.50	4.67
		N=13 R=0.981	2	G	7.05	6.00
		X MEAN=3.594 Y MEAN=4.391	3	C	3.23	2.03
		Y=0.590+1.058X	4	C	1.52	1.02
		ADJUSTED SLOPE=1.179	5	G	4.13	3.38
			6	C	1.72	1.12
			7	G	3.08	2.01
			8	B	2.03	1.74
			9	G	6.20	5.70
			10	B	2.19	1.24

Table III (continued)

Mirror Number*	Type†	Archaeological Provenance	Analysis Number	Surface Condition‡	SnKα / CuKβ	PbLγ / CuKβ
			11	G	5.39	4.53
			12	G	9.56	7.69
			13	G	5.48	5.59
32	B	Saga Prefecture	1	B	2.06	0.56
		N=13 R=0.644	2	C	0.61	0.17
		X MEAN=0.686 Y MEAN=1.635	3	G	1.09	0.53
		Y=0.712+1.346X	4	C	1.88	0.79
		ADJUSTED SLOPE=2.095	5	C	1.69	0.59
		"C" Data Only:	6	B	3.48	1.13
		N=6 R=0.965	7	B	1.43	0.88
		X MEAN=0.410 Y MEAN=1.013	8	C	0.30	0.20
		Y=−0.005+2.483X	9	C	0.49	0.21
		ADJUSTED SLOPE=2.475	10	C	1.11	0.50
			11	B	2.30	1.44
			12	B	2.04	1.50
			13	B	2.78	0.42
33	B	Saga Prefecture	1	C	0.65	0.51
		N=13 R=0.825	2	G	0.54	0.56
		X MEAN=0.706 Y MEAN=0.616	3	C	0.60	0.37
		Y=−0.088+0.997X	4	G	0.27	0.40
		ADJUSTED SLOPE=0.902	5	C	0.45	0.23
		"C" Data Only:	6	G	0.50	0.56
		N=3 R=0.961	7	G	1.95	1.65
		X MEAN=0.370 Y MEAN=0.567	8	G	0.10	0.43
		Y=0.302+0.714X	9	B	0.67	0.70
		ADJUSTED SLOPE=1.460	10	B	0.85	1.05
			11	G	1.10	1.32
			12	G	0.14	0.80
			13	G	0.19	0.60
34	B	Saga Prefecture	1	C	0.58	0.56
		N=13 R=0.824	2	C	0.65	0.57
		X MEAN=0.348 Y MEAN=0.425	3	G	0.14	0.26
		Y=0.071+1.017X	4	G	0.22	0.13
		ADJUSTED SLOPE=1.177	5	C	0.64	0.42
			6	G	0.16	0.15
			7	G	0.19	0.12
			8	C	0.71	0.45
			9	G	0.29	0.15
			10	G	0.19	0.18
			11	G	0.41	0.60
			12	C	0.57	0.36
			13	C	0.77	0.57
35	B	Saga Prefecture	1	G	5.89	2.19
		N=10 R=0.938	2	G	5.13	1.92
		X MEAN=1.477 Y MEAN=3.723	3	G	6.30	2.75
		Y=0.198+2.387X	4	C	2.68	0.86
		ADJUSTED SLOPE=2.498	5	G	0.89	0.45
			6	G	1.47	0.85
			7	B	4.08	1.48
			8	B	4.13	1.25
			9	B	3.50	1.78
			10	B	3.16	1.24
36	B	Saga Prefecture	1	B	4.63	3.16
		N=14 R=0.834	2	B	2.91	1.99
		X MEAN=2.979 Y MEAN=5.077	3	B	3.79	1.95
		Y=0.389+1.574X	4	B	5.85	4.00
		ADJUSTED SLOPE=1.691	5	B	5.95	3.45
			6	G	7.30	2.40
			7	C	1.44	1.18
			8	G	7.63	5.02
			9	B	5.50	3.29
			10	B	5.64	3.36
			11	G	2.69	1.98
			12	G	6.00	3.55
			13	B	8.00	4.00
			14	B	3.75	2.38
37	B	Saga Prefecture	1	G	1.43	0.99
		N=14 R=0.972	2	B	2.08	1.27
		X MEAN=1.269 Y MEAN=2.110	3	B	2.86	2.00
		Y=0.265+1.454X	4	G	0.77	0.43
		ADJUSTED SLOPE=1.633	5	G	0.85	0.42
			6	G	2.39	1.26
			7	B	1.50	0.88
			8	B	3.15	2.00
			9	B	3.27	2.04
			10	B	1.38	0.69
			11	B	2.68	1.66
			12	B	2.78	1.43
			13	B	2.24	1.38
			14	B	2.16	1.31
38	A	Gunma Prefecture	1	G	0.77	0.12
		N=4 R=0.298	2	G	1.23	0.31
		X MEAN=0.220 Y MEAN=0.720	3	G	0.51	0.17
		Y=0.444+1.256X	4	C	0.37	0.28
		ADJUSTED SLOPE=3.046				
39	A	Hyōgo Prefecture	1	C	0.53	0.61
		N=10 R=0.880	2	C	0.53	0.52
		X MEAN=0.609 Y MEAN=0.555	3	G	0.95	1.14
		Y=0.045+0.838X	4	G	0.84	0.90
		ADJUSTED SLOPE=0.898	5	G	0.25	0.17
			6	G	0.44	0.51
			7	G	0.70	0.81
			8	B	0.21	0.21
			9	C	0.89	0.69
			10	B	0.21	0.53
40	A	Hyōgo Prefecture	1	C	0.58	0.32
		N=10 R=0.983	2	C	0.50	0.20
		X MEAN=0.376 Y MEAN=0.654	3	B	0.44	0.21
		Y=0.197+1.215X	4	B	0.39	0.21
		ADJUSTED SLOPE=1.585	5	C	0.37	0.19
			6	G	0.56	0.30
			7	G	0.47	0.25
			8	G	0.90	0.58
			9	G	1.32	0.89
			10	G	1.01	0.71

TABLE III (continued)

Mirror Number*	Type†	Archaeological Provenance	Analysis Number	Surface Condition‡	SnKα/CuKβ	PbLγ/CuKβ
41	B	Hyōgo Prefecture	1	C	1.16	0.52
		N=10 R=0.986	2	C	0.89	0.38
		X MEAN=0.423 Y MEAN=0.910	3	C	0.79	0.34
		Y=0.150+1.798X	4	B	0.79	0.39
		ADJUSTED SLOPE=2.092	5	G	1.22	0.58
			6	G	0.32	0.15
			7	G	1.41	0.74
			8	G	0.45	0.17
			9	G	1.33	0.67
			10	C	0.74	0.29
42	A	Kyōto–Nara Prefecture?	1	G	1.17	0.73
		N=14 R=0.927	2	G	0.11	0.03
		X MEAN=0.219 Y MEAN=0.364	3	G	0.16	0.04
		Y=0.082+1.283X	4	G	0.28	0.06
		ADJUSTED SLOPE=1.480	5	G	0.31	0.11
			6	G	0.28	0.22
			7	G	0.21	0.11
			8	G	0.30	0.11
			9	G	0.21	0.09
			10	G	0.16	0.17
			11	G	0.61	0.39
			12	G	0.82	0.60
			13	G	0.26	0.09
			14	G	0.21	0.32
43	A	Hyōgo Prefecture	1	C	0.72	0.84
		N=11 R=0.379	2	C	0.49	0.41
		X MEAN=0.819 Y MEAN=0.455	3	C	0.44	0.47
		Y=0.255+0.244X	4	G	0.27	0.83
		ADJUSTED SLOPE=0.523	5	G	0.37	0.79
			6	G	0.44	0.70
			7	G	0.62	1.42
			8	G	0.33	0.61
			9	G	0.56	1.19
			10	G	0.08	0.78
			11	C	0.69	0.97
44	A	Fukuoka Prefecture	1	G	0.49	0.31
		N=5 R=−0.116	2	B	1.32	1.16
		X MEAN=0.860 Y MEAN=0.548	3	B	0.63	0.46
		Y=0.608+ −0.070X	4	G	0.23	0.23
		ADJUSTED SLOPE=0.346	5	B	0.07	2.14
		Without Analysis No. 5:				
		N=4 R=0.986				
		X MEAN=0.540 Y MEAN=0.668				
		Y=0.083+1.082X				
		ADJUSTED SLOPE=1.188				
45	A	Fukuoka Prefecture	1	G	0.13	0.63
		N=5 R=0.397	2	G	0.15	0.51
		X MEAN=0.492 Y MEAN=0.228	3	G	0.63	0.59
		Y=−0.117+0.700X	4	G	0.06	0.42
		ADJUSTED SLOPE=0.476	5	G	0.17	0.31
46	A	Fukuoka Prefecture	1	G	0.15	1.11
		N=5 R=−0.707	2	G	0.39	0.54
		X MEAN=1.186 Y MEAN=0.208	3	G	0.13	2.36
		Y=0.332+ −0.104X	4		0.14	1.34
		ADJUSTED SLOPE=0.109	5	G	0.23	0.58
47	A	Fukuoka Prefecture	1	G	0.20	0.33
		N=5 R=0.725	2	G	1.08	1.11
		X MEAN=0.620 Y MEAN=0.406	3	G	0.36	0.28
		Y=−0.104+0.822X	4	G	0.20	0.63
		ADJUSTED SLOPE=0.687	5	G	0.19	0.75
48	A	Fukuoka Prefecture	1	G	0.12	0.40
		N=4 R=0.246	2	G	0.31	4.68
		X MEAN=1.612 Y MEAN=0.250	3	G	0.43	0.50
		Y=0.222+0.018X	4	B	0.14	0.87
		ADJUSTED SLOPE=0.080				
49	A	Ōsaka Prefecture	1	C	0.33	0.25
		N=5 R=0.986	2	C	0.30	0.24
		X MEAN=0.606 Y MEAN=0.594	3	C	0.35	0.36
		Y=0.154+0.727X	4	G	1.30	1.61
		ADJUSTED SLOPE=0.874	5	G	0.69	0.57
50	A	Ōsaka Prefecture	1	C	0.19	0.19
		N=5 R=0.118	2	G	0.19	0.25
		X MEAN=0.278 Y MEAN=0.194	3	G	0.22	0.22
		Y=0.184+0.037X	4	G	0.15	0.31
		ADJUSTED SLOPE=0.645	5	G	0.22	0.42
51	A	Ōsaka Prefecture	1	C	0.24	0.15
		N=5 R=0.813	2	G	0.27	0.66
		X MEAN=0.306 Y MEAN=0.208	3	C	0.21	0.18
		Y=0.156+0.170X	4	C	0.19	0.14
		ADJUSTED SLOPE=0.540	5	C	0.22	0.33
		"C" Data Only:				
		N=4 R=0.181				
		X MEAN=0.200 Y MEAN=0.215				
		Y=0.206+0.043X				
		ADJUSTED SLOPE=0.945				
52	A	Ōsaka Prefecture	1	C	0.25	0.58
		N=5 R=0.625	2	G	0.21	0.41
		X MEAN=0.540 Y MEAN=0.184	3	G	0.12	0.25
		Y=0.109+0.050X	4	G	0.11	0.44
		ADJUSTED SLOPE=0.503	5	G	0.23	1.02
53	A	Ōsaka Prefecture	1	C	0.24	0.31
		N=10 R=0.668	2	B	0.33	0.36
		X MEAN=0.540 Y MEAN=0.263	3	G	0.31	0.69
		Y=0.179+0.054X	4	G	0.15	0.38
		ADJUSTED SLOPE=0.410	5	G	0.21	0.49
			6	C	0.39	1.34
			7	C	0.30	0.66
			8	C	0.20	0.52
			9	C	0.29	0.37
			10	G	0.21	0.28
54	B	Ōsaka Prefecture	1	C	0.20	0.29
		N=6 R=−0.114	2	C	0.22	0.63

TABLE III (continued)

Mirror Number*	Type†	Archaeological Provenance	Analysis Number	Surface Condition‡	$\frac{\mathrm{SnK}\alpha}{\mathrm{CuK}\beta}$	$\frac{\mathrm{PbL}\gamma}{\mathrm{CuK}\beta}$
		X MEAN=0.398 Y MEAN=0.255	3	B	0.24	0.44
		Y=0.269+0.043X	4	G	0.30	0.31
		ADJUSTED SLOPE=0.575	5	C	0.31	0.47
		"C" Data Only:	6	C	0.26	0.25
		N=4 R=0.055				
		X MEAN=0.410 Y MEAN=0.248				
		Y=0.241+0.015X				
		ADJUSTED SLOPE=0.533				
55	A	Ōsaka Prefecture	1	C	0.14	0.19
		N=6 R=0.359	2	C	0.15	0.24
		X MEAN=0.258 Y MEAN=0.157	3	G	0.22	0.24
		Y=0.119+0.145X	4	G	0.15	0.27
		ADJUSTED SLOPE=0.563	5	B	0.11	0.18
			6	C	0.17	0.43
56	A	Ōsaka Prefecture	1	C	0.19	0.33
		N=7 R=−0.244	2	G	0.16	0.30
		X MEAN=0.753 Y MEAN=0.164	3	G	0.10	0.64
		Y=0.172+−0.011X	4	G	0.15	0.56
		ADJUSTED SLOPE=0.085	5	G	0.15	2.90
			6	G	0.16	0.22
			7	G	0.24	0.32
57	A	Ōsaka Prefecture	1	C	0.12	0.23
		N=6 R=0.881	2	C	0.21	0.66
		X MEAN=0.552 Y MEAN=0.167	3	G	0.21	0.97
		Y=0.076+0.164X	4	G	0.21	0.66
		ADJUSTED SLOPE=0.279	5	G	0.10	0.32
			6	C	0.15	0.47
58	A	Kyōto Prefecture	1	G	8.92	4.25
		N=7 R=0.868	2	G	6.56	3.75
		X MEAN=2.583 Y MEAN=3.666	3	G	1.07	0.71
		Y=−1.455+1.983X	4	G	3.95	2.45
		ADJUSTED SLOPE=1.529	5	G	1.20	1.44
			6	G	3.44	3.80
			7	G	0.52	1.68
59	A	Ōsaka Prefecture	1	C	0.24	0.24
		N=7 R=0.968	2	C	0.26	0.31
		X MEAN=0.527 Y MEAN=0.344	3	C	0.21	0.24
		Y=0.103+0.457X	4	C	0.31	0.39
		ADJUSTED SLOPE=0.569	5	B	0.25	0.26
			6	G	0.87	1.60
			7	C	0.27	0.65
60	A	Fukuoka Prefecture	1	G	0.44	0.38
		N=11 R=0.360	2	B	0.28	0.16
		X MEAN=0.212 Y MEAN=0.318	3	G	0.30	0.18
		Y=0.219+0.469X	4	B	0.35	0.17
		ADJUSTED SLOPE=1.384	5	G	0.09	0.16
			6	G	0.46	0.22
			7	G	0.30	0.14
			8	B	0.43	0.22
			9	B	0.26	0.33
			10	G	0.31	0.13
			11	B	0.28	0.24
61	B	Ōsaka Prefecture	1	G	0.69	1.66
		N=13 R=0.925	2	G	0.29	0.62
		X MEAN=0.926 Y MEAN=0.394	3	G	0.33	0.59
		Y=0.089+0.329X	4	G	0.28	0.59
		ADJUSTED SLOPE=0.412	5	G	0.38	0.82
			6	G	0.47	1.16
			7	G	0.36	0.74
			8	G	0.59	1.25
			9	G	0.40	0.95
			10	G	0.14	0.20
			11	G	0.46	1.36
			12	G	0.37	0.94
			13	G	0.36	1.16
62	B	Kyōto Prefecture	1	C	1.72	1.08
		N=13 R=0.953	2	G	0.94	0.54
		X MEAN=0.825 Y MEAN=1.339	3	C	1.62	0.89
		Y=−0.502+2.233X	4	G	0.47	0.37
		ADJUSTED SLOPE=1.677	5	G	0.49	0.52
			6	C	1.37	0.82
			7	C	1.56	0.91
			8	C	1.37	0.78
			9	G	0.40	0.52
			10	C	1.53	0.96
			11	C	1.61	1.05
			12	G	2.57	1.23
			13	C	1.76	1.05
63	B	Tottori Prefecture	1	G	0.56	0.41
		N=10 R=0.940	2	G	1.24	0.91
		X MEAN=0.588 Y MEAN=0.706	3	G	1.23	1.03
		Y=0.041+1.131X	4	G	0.40	0.35
		ADJUSTED SLOPE=1.188	5	G	0.76	0.59
			6	G	0.86	0.59
			7	G	0.38	0.30
			8	G	0.77	0.79
			9	G	0.74	0.81
			10	G	0.12	0.10
64	B	Saga Prefecture	1	G	0.44	1.69
		N=10 R=0.970	2	G	0.38	1.26
		X MEAN=1.307 Y MEAN=0.365	3	G	0.44	1.41
		Y=0.029+0.257X	4	G	0.48	1.74
		ADJUSTED SLOPE=0.277	5	G	0.56	2.09
			6	G	0.31	1.05
			7	G	0.21	0.85
			8	G	0.18	0.59
			9	G	0.32	1.05
			10	G	0.33	1.34
65	B	Saga Prefecture	1	B	1.13	3.02
		N=10 R=0.949	2	B	1.95	4.81
		X MEAN=1.853 Y MEAN=0.753	3	B	1.14	3.80
		Y=0.087+0.360X	4	B	1.43	2.53
		ADJUSTED SLOPE=0.387	5	G	0.71	2.25
			6	G	0.38	0.58
			7	G	0.20	0.35
			8	G	0.20	0.34

TABLE III (continued)

Mirror Number*	Type†	Archaeological Provenance	Analysis Number	Surface Condition‡	$\frac{SnK\alpha}{CuK\beta}$	$\frac{PbL\gamma}{CuK\beta}$
			9	G	0.19	0.52
			10	G	0.20	0.33
66	B	Saga Prefecture	1	G	0.15	0.30
		N=10 R=0.933	2	G	0.11	0.19
		X MEAN=1.166 Y MEAN=0.349	3	G	0.17	0.34
		Y=0.103+0.210X	4	G	0.24	0.76
		ADJUSTED SLOPE=0.264	5	G	0.16	0.27
			6	G	0.35	0.92
			7	G	0.47	1.71
			8	G	0.69	2.88
			9	G	0.69	1.94
			10	G	0.46	2.35
67	B	Saga Prefecture	1	G	0.26	0.43
		N=10 R=0.780	2	G	0.30	0.61
		X MEAN=0.446 Y MEAN=0.243	3	G	0.27	0.47
		Y=0.069+0.390X	4	G	0.30	0.57
		ADJUSTED SLOPE=0.539	5	G	0.22	0.40
			6	G	0.27	0.41
			7	G	0.20	0.36
			8	G	0.17	0.29
			9	G	0.25	0.45
			10	G	0.19	0.47
68	A	Saga Prefecture	1		0.12	0.08
		N=6 R=0.473	2		0.13	0.14
		X MEAN=0.262 Y MEAN=0.155	3		0.13	0.20
		Y=0.129+0.100X	4		0.15	0.15
		ADJUSTED SLOPE=0.422	5		0.16	0.64
		Without Analysis No. 5:	6		0.24	0.36
		N=5 R=0.930				
		X MEAN=0.186 Y MEAN=0.154				
		Y=0.074+0.432X				
		ADJUSTED SLOPE=0.748				
69	A	Saga Prefecture	1		0.28	0.39
		N=5 R=0.831	2		0.14	0.05
		X MEAN=0.176 Y MEAN=0.206	3		0.14	0.06
		Y=0.112+0.532X	4		0.33	0.25
		ADJUSTED SLOPE=0.945	5		0.14	0.13
		Without Analysis No. 4:				
		N=4 R=0.975				
		X MEAN=0.158 Y MEAN=0.175				
		Y=0.107+0.429X				
		ADJUSTED SLOPE=0.817				
70	A	Nara Prefecture	1	G	0.92	1.12
		N=15 R=0.948	2	G	1.07	1.47
		X MEAN=1.264 Y MEAN=1.144	3	G	0.45	0.51
		Y=0.050+0.865X	4	G	1.12	1.30
		ADJUSTED SLOPE=0.898	5	G	2.14	2.58
			6	G	2.16	2.41
			7	G	1.10	1.16
			8	G	1.00	0.81
			9	G	0.92	1.10
			10	B	1.33	1.35
			11	G	1.78	1.53
			12	G	1.21	1.15
			13	G	0.45	0.63
			14	G	1.06	1.24
			15	G	0.45	0.60
71	A	Nara Prefecture	1	G	2.92	2.58
		N=17 R=0.974	2	G	3.72	3.48
		X MEAN=2.212 Y MEAN=2.435	3	G	1.96	1.90
		Y=0.266+0.981X	4	G	0.61	0.41
		ADJUSTED SLOPE=1.056	5	G	0.67	0.56
			6	G	1.06	0.75
			7	G	1.01	0.69
			8	G	4.53	4.00
			9	G	0.99	0.70
			10	G	0.57	0.38
			11	G	0.70	0.45
			12	G	2.46	2.23
			13	G	2.84	2.25
			14	G	1.80	2.28
			15	G	6.00	6.00
			16	G	5.18	3.94
			17	G	4.38	5.00
72	B	Nara Prefecture	1	G	0.22	0.24
		N=16 R=0.794	2	C	0.23	0.27
		X MEAN=0.251 Y MEAN=0.228	3	C	0.22	0.23
		Y=0.036+0.764X	4	C	0.23	0.28
		ADJUSTED SLOPE=0.906	5	G	0.22	0.24
		"C" Data Only:	6	G	0.22	0.25
		N=5 R=0.975	7	G	0.23	0.24
		X MEAN=0.254 Y MEAN=0.224	8	G	0.20	0.23
		Y=0.155+0.272X	9	G	0.22	0.25
		ADJUSTED SLOPE=0.875	10	G	0.22	0.24
			11	C	0.23	0.28
			12	C	0.21	0.21
			13	G	0.20	0.22
			14	G	0.22	0.26
			15	G	0.26	0.25
			16	G	0.31	0.32
73	B	Kyōto–Nara Prefecture?	1	G	0.09	0.23
		N=12 R=0.471	2	G	0.16	0.42
		X MEAN=0.578 Y MEAN=0.150	3	G	0.09	0.20
		Y=0.092+0.099X	4	G	0.19	0.45
		ADJUSTED SLOPE=0.232	5	G	0.19	0.46
			6	G	0.23	0.86
			7	G	0.25	0.94
			8	G	0.18	0.58
			9	G	0.08	0.38
			10	G	0.10	0.66
			11	G	0.12	0.69
			12	G	0.12	1.07
74	B	Kyōto–Nara Prefecture?	1		0.24	0.23
		N=15 R=0.849	2		0.11	0.26
		X MEAN=0.249 Y MEAN=0.182	3		0.43	0.41
		Y=0.067+1.000X	4		0.10	0.19
		ADJUSTED SLOPE=0.775	5		0.40	0.52

Table III (continued)

Mirror Number*	Type†	Archaeological Provenance	Analysis Number	Surface Condition‡	SnKα/CuKβ	PbLγ/CuKβ
			6		0.17	0.26
			7		0.02	0.12
			8		0.01	0.21
			9		0.13	0.27
			10		0.06	0.12
			11		0.07	0.09
			12		0.23	0.25
			13		0.30	0.23
			14		0.11	0.19
			15		0.35	0.39
75	B	Kyōto Prefecture	1	B	0.77	0.49
		N=6 R=0.955	2	B	0.71	0.52
		X MEAN=0.682 Y MEAN=1.128	3	B	1.02	0.71
		Y= −0.038+1.710X	4	G	2.18	1.29
		ADJUSTED SLOPE=1.663	5	C	0.82	0.49
			6	C	1.27	0.59
76	B	Nara Prefecture	1	G	0.27	0.07
		N=12 R= −0.535	2	G	0.25	0.09
		X MEAN=0.084 Y MEAN=0.260	3	G	0.22	0.09
		Y=0.337+ −0.916X	4	G	0.25	0.10
		ADJUSTED SLOPE=2.512	5	G	0.26	0.10
			6	G	0.26	0.09
			7	G	0.26	0.08
			8	G	0.28	0.08
			9	G	0.25	0.08
			10	G	0.28	0.07
			11	G	0.26	0.08
			12	G	0.28	0.08
77	B	Nara Prefecture	1	B	0.74	0.47
		N=13 R=0.985	2	B	0.62	0.32
		X MEAN=1.032 Y MEAN=1.656	3	G	1.30	0.58
		Y=0.299+1.315X	4	G	0.85	0.48
		ADJUSTED SLOPE=1.434	5	G	0.80	0.49
			6	B	0.65	0.35
			7	G	0.36	0.24
			8	G	1.17	0.61
			9	B	0.69	0.43
			10	G	1.24	0.64
			11	G	3.82	2.09
			12	G	6.29	4.86
			13	G	3.00	1.86
78	B	Ōsaka Prefecture	1	B	0.46	1.20
		N=14 R=0.871	2	G	0.55	1.57
		X MEAN=1.344 Y MEAN=0.496	3	G	0.69	2.10
		Y=0.201+0.219X	4	G	0.58	1.75
		ADJUSTED SLOPE=0.356	5	G	0.53	1.63
			6	G	0.51	1.75
			7	G	0.45	1.06
			8	G	0.54	1.67
			9	G	0.47	1.09
			10	B	0.40	0.83
			11	B	0.35	1.10
			12	C	0.34	0.72
			13	B	0.40	0.80
			14	G	0.67	1.54
79	A	Kyōto Prefecture	1	C	0.53	0.86
		N=7 R=0.965	2	G	1.95	1.85
		X MEAN=0.797 Y MEAN=0.807	3	G	0.26	0.16
		Y=0.074+0.920X	4	G	0.41	0.34
		ADJUSTED SLOPE=0.978	5	G	0.42	0.29
			6	G	0.65	0.52
			7	G	1.43	1.56

EARLY CHINESE BLACK MIRRORS AND PATTERN-ETCHED WEAPONS

By W. T. CHASE*
and URSULA MARTIUS FRANKLIN**

INTRODUCTION

Among the bronze mirrors produced in China during the Chou and Han periods, some exhibit shiny black surfaces. Black shiny surface finish is not uncommon among Chinese mirrors, but also not universal; some of the mirrors recently discovered in controlled archaeological excavations in the People's Republic of China have the characteristic black appearance; others do not. In some instances both black and non-black mirrors have been found in the same tomb and burial environment.

Mirrors with the shiny black surface are unusually corrosion-resistant. When corrosion occurs, it does so in a very typical manner; the surface of the object is not attacked uniformly. It appears to crack or splinter locally and corrosion occurs from underneath. The corrosion products form small and isolated pockets within the still unattacked original surface. They look like warts or chicken pox; every observer emphasizes this phenomenon. The blisters contain the normal green copper salts that one finds on corroding bronzes. Frequently, as corrosion proceeds, it lifts the shiny surface above the corrosion products.

Black mirrors share other common characteristics; they show a glossy, often jet-black (sometimes dark green or brown) surface on the face of the mirror and on undecorated areas of the back. Usually the black is shiny, with a vitreous luster. The relief-decorated portion of the back is also black, but it appears dull. The loop in the center of the back is evenly black, both on its top and underside. The mirror back underneath the loop is black as well. Visual inspection of the decorated back reveals no discontinuities of the black surface within the ornamentation, although relief decor can be quite deep and complex. On the plain face one can often detect polishing marks *under* the shiny surface layer.

Mirrors with the shiny black surface are not limited to one particular style or period. Most of the known late Chou mirror types can be found with the black surface. Black mirrors range in date from Middle Chou through Han to T'ang,[1] although we are not sure that all the dark finishes found on mirrors, especially the post-Han mirrors, are of the same chemical and mechanical nature as on the earlier material. Furthermore, the characteristic black surface is not restricted to mirrors: some weapons and utensils also show similar glossy, dark and highly corrosion-resistant surfaces.

Is this special surface the accidental result of environmental conditions, or is it an intentional surface finish, purposely produced by the ancient craftsmen? If it is a natural corrosion product, is its special color and chemical inactivity due to some inherent

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[1] See below, section entitled "Geographical and Chronological Limits of Black Mirrors."

property of the metal, or solely to environmental conditions?

If it is, on the other hand, an intentional surface finish, is it the result of special casting conditions and/or metal composition, or is it a post-manufacture, or possibly a post-use, process? How was it produced? What were the reasons for the special surface finish?

BLACK-SURFACED MIRRORS

PREVIOUS INVESTIGATIONS

By providing technical details on the structure and composition of the ancient objects, a number of investigators have attempted to answer the above questions. In this century, the first study in English was that by Orvar Karlbeck in 1926. His article simply stated, "Some specimens are coated with black or brown lacquer and others show traces of beaten gold."[2] Since then, the "black lacquer" designation has been applied often to characterize certain mirrors; no one has yet put forward technical evidence for the presence of lacquer; its absence has, however, been specifically reported.[3]

One exception to this statement is the recent study by Bulling and Drew.[4] While not specifically concerned with *black* mirrors, the authors report the presence of dark lacquers that they consider as being applied well after the manufacture and use of the mirrors; however they provided no experimental evidence.[5]

In 1931, Yetts addressed the question of the black bronze mirrors quite specifically.[6] He expressed strong criticism of Collins' just-published paper on corrosion of early Chinese bronzes.[7] Collins stated his opinion that the black mirror surfaces had obtained their particular properties as a consequence of special environmental factors. He considered the black surface to be a natural patination resulting in a very stable form of cuprite of unknown morphology. To this, Yetts replied:

> I have long held the view that the quality of this coating is so perfect and uniform that the generally accepted explanation of a patina due to accidental changes of environment fails to carry conviction. At my request, Dr. H. J. Plenderleith has been good enough to make a chemical examination and he finds that the black coating withstands all reagents except a mixture of nitric and hydrofluoric acids. This fact suggests the possibility that the coating may have been intentionally produced by

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[2] Orvar Karlbeck, "Notes on Some Early Chinese Mirrors," *The China Journal of Science and Arts*, vol. 4, no. 1 (1926), pp. 3–9.

[3] Rutherford J. Gettens, "Some Observations Concerning the Lustrous Surface on Ancient Eastern Bronze Mirrors," *Technical Studies in the Field of Fine Arts*, vol. 3 (1934), pp. 29–37; *idem*, "Tin-oxide Patina of Ancient High-tin Bronze," *The Bulletin of the Fogg Museum of Art*, vol. 11, no. 1 (1949), pp. 16–26; see esp. p. 19.

[4] A. Gutkind Bulling and Isabella Drew, "The Dating of Chinese Bronze Mirrors," *Archives of Asian Art*, vol. 25 (1971–1972), p. 38; *MASCA Newsletter*, vol. 7, no. 1 (June, 1971), pp. 2–3.

[5] One of the authors (WTC), while examining Chinese bronze mirrors in the storage of the Field Museum, Chicago, in 1977, found one that appeared to be lacquered. The coating was thick and brownish, it looked quite different from the black-surfaced mirrors in the same drawer. The object was not sampled or analyzed, however.

[6] W. Perceval Yetts, "Problems of Chinese Bronzes," *Journal of the Royal Central Asian Society*, vol. 18, part 3. (August 1931), pp. 399–402.

[7] William F. Collins, "The Corrosion of Early Chinese Bronzes," *Journal of the Institute of Metals*, vol. 45 (1931), pp. 23–55.

> mixing siliceous matter with the layer of the mold which comes into direct contact with the molten metal. Thus, a coating of a compound somewhat like silicon bronze may be produced. The problem must be investigated further before any definite statement can be made.

Unfortunately, neither Yetts nor Plenderleith himself did provide further details. Plenderleith simply stated that he detected silica in amounts large enough to convince him that it was intentionally introduced, but he did not elaborate on how the color and properties of the mirrors could be related to the presence of SiO_2.[8]

In 1934, both Collins[9] and Gettens[10] gave the black mirrors more detailed attention. Their papers, appearing almost simultaneously and apparently independently, are the first technical studies of the black bronze surfaces. While Gettens restricted himself to mirrors, Collins analyzed, in addition to mirrors, a sword fragment and a Korean bronze bowl. Gettens' interest in mirrors had been aroused initially by the objects in the Hoyt Collection at the Fogg Art Museum; later he was to obtain access to the mirrors of the James Marshall Plumer collection, which allowed him to broaden significantly his experimental base.

Collins was a mining engineer, not a professional sinologist; in addition to including analyses from the Japanese literature, he used objects that he had collected in China.[11] While Gettens kept reprints and excerpts from Collins' papers and quoted Collins in publication, there is no evidence that the two ever met or corresponded. One cannot help speculating on what would have happened if these two men had had an opportunity for collaboration. Their work is strikingly similar.

Both were basically experimentalists, doing their own microscopy and chemical analyses. Collins used the laboratories at the British Museum and at Imperial College; Gettens used those at the Fogg Art Museum and the Harvard University Chemistry Department. Both pointed to the characteristic corrosion on the mirrors, both reported the absence of mercury and organic materials. Their chemical analyses agreed: both reported mirror bronze composition around 70–75% copper, 20–25% tin, 1–5% lead. Both documented the inertness of the mirrors' surfaces to chemical attack by cold acids and alkaline solutions, and both illustrated metallographic cross sections in which the surface layers exhibited continuous and gradual transition into the body of the metal.

Collins stated very clearly that it was the α-phase of the alloy that was altered at and below the surface. In addition to the examination of cross sections, he also examined a mirror normally to the black surface; first in its original condition, and then after each increment of polishing down the surface until the unaltered bronze was reached. He observed that the surface material completely lacked any discernible grain structure and that the alteration products (which Collins thought to be cuprite) penetrated deeply into the interior of the mirrors. Collins coined the term "rooted" in this context.

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[8] Harold J. Plenderleith, "Technical Notes on Chinese Bronzes with Special Reference to Patina and Incrustation," *Transactions of the Oriental Ceramic Society*, vol. 6 (1938–1939), pp. 33–55.

[9] William F. Collins, "The Mirror-black and 'Quicksilver' Patinas of Certain Chinese Bronzes," *Journal of the Royal Anthropological Society of Great Britain and Ireland*, vol. 64 (1934), pp. 69–79.

[10] Gettens, "Some Observations . . ."

[11] In his 1931 paper on corrosion, read at the Institute of Metals by C. H. Desch in the author's absence, Collins was identified as "Agent in Peking of the Anglo-French China Corporation and S. Pearson and Sons (Contracting Department)."

Both Gettens and Collins noticed that the mirrors were in the "as-cast" condition, and both saw the presence of redeposited copper in the matrices. In an unconscious parallelity of approach, both men turned to the then novel X-ray diffraction technique for help in the identification of the unknown product on the mirrors' surface.

Here their work diverged. Ironically, both seem to have missed a major point of information. The surface layer of black mirrors is very difficult to remove; the first X-ray diffraction patterns obtained for Gettens by J. Norton at the Massachusetts Institute of Technology showed very weak and diffuse lines that do not appear to correspond to any simple pattern.[12] Later, Gettens dissolved the material removed from the surface by boiling it in concentrated hydrofluoric acid. He found that the residue, which remained after evaporation of the acid, showed the presence of tin in a microchemical test. He does not seem to have tested for any other elements. In 1949 Gettens tried again to obtain X-ray evidence. He reports that:

> Samples weighing about 1 mg were scraped from the smooth surfaces of two mirror fragments and these were leached with 1-to-1 hydrochloric acid to dissolve out copper compounds and any traces of iron that might have got into the sample from abrasion of the sampling tool. After careful washing, the samples were compared microscopically with the untreated samples and they appeared not to have been physically altered by the treatment. X-ray diffraction pictures were then taken.

The X-ray diffraction patterns again showed broad lines, but they could be measured and identified. They corresponded closely or exactly to the patterns of artificially prepared stannic oxide, though not to the pattern of the mineral cassiterite.[13]

Gettens also noticed a difference in the optical properties of the mirrors' surfaces and those of cassiterite. He had found the mirrors' surfaces to be quite homogeneous and measured the refractive index on several of them. It ranged from $n = 1.78$ to $n = 1.81$. Cassiterite, on the other hand, is tetragonal, with $\omega = 1.997$ and $\epsilon = 2.093$.

The evidence of tin oxide led Gettens to believe, from then on, that the unique properties of the black mirrors were due to a special tin oxide patina, a variant of the "water patina" often found on ceremonial bronze vessels. He admitted freely that the color, the subsequent mode of cracking and corrosion attack, as well as the chemical stability of the black surface layers were difficult to explain on this basis.

Collins, on the other hand, had established in his general study of the corrosion of bronzes that the first corrosion product of ancient bronzes was cuprite. This was done for him by X-ray diffraction carried out at the British Museum by F. A. Bannister. Seeing no fundamental difference between the metallographic structure of the black high-tin bronze mirrors and other bronzes of similar composition, and believing that the black surfaces were natural occurrences, Collins found himself faced with the need to reconcile the color and the composition as cuprite. He summarized his conclusions as follows:

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[12] Gettens, "Some Observations . . ."

[13] Gettens, "Tin-oxide . . .", p. 22

> 1. The (mirror-black) patina of certain early Chinese bronzes consists of crystalline cuprite (cuprous oxide, Cu_2O) of unusual mineral structure, possibly having a thin film of tenorite (black cupric oxide, CuO) on its surface. Bronzes bearing this patina are usually of silver-white or nearly white metal, with chemical composition and crystallographic structure closely resembling . . . speculum metal . . . .
> 2. Speculum metal appears to owe its 'rustless' property to its high proportion of fine-grained duplex (alpha plus delta structure). The resistance to corrosion of the cuprite which grows out of it and upon it, may be due to the like structure acquired from its parent alloy. (Under natural conditions, some massive crystals of cuprite alter on their crystal faces to malachite and thus acquire a green 'patina'. Others do not. It is not known exactly why such alterations occur or are arrested.)
> 3. The unusually fine lustre and polished appearance of this patina are due: (a) To original polishing of the bronze . . . (b) To thinness and evenness of the corrosion layer.[14]

This explanation does not at all deal with the fact that there are many Chinese mirrors of the same overall composition which, in fact, have no black surface layers and do not exhibit corrosion-resistant behavior.

Both Gettens and Collins were aware that Plenderleith had found silicon on the black surfaces. But the comment by Yetts—that something like an inert surface layer of silicon bronze could have been produced—may have distracted them from the significance of this information. Gettens pointedly emhasized that "there is no evidence of the formation of any compound like a silicon bronze . . ."[15] If Yetts had not used the term "silicon bronze", which had a much more precise meaning to Gettens and Collins than it may have had to him, then the matter might not have rested here, but it did.

PRESENT INVESTIGATIONS

When, in 1960, one of the present authors (UMF) began to look again at the black mirror problem, it was on the suggestion of the late W. Todd, then chief conservator at the Royal Ontario Museum in Toronto, who was fascinated by the corrosion-resistance of the black bronzes. At that time new experimental techniques such as electron microprobe analysis and X-ray fluorescence made a fresh look at the vexing problem of dark bronze surfaces worthwhile.

The initial samples used were fragments from Han mirrors from the Royal Ontario Museum study collection. Later Gettens put his samples at the disposal of UMF. Basically, the studies included optical investigations and X-ray and electron microprobe studies, as well as determination of density and hardness.

In order to show the nature and results of our investigations we have chosen two examples for this article to illustrate typical "cases." The descriptions on Figure 1 (Mirror #1) and Figure 2 (Mirror #4) come from the catalogue cards in the Royal Ontario Museum. Both figures show the mirrors in present condition, after sampling.

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[14] Collins, "The Mirror-black . . .", pp. 77–78

[15] Gettens, "Some Observations . . .", p. 36

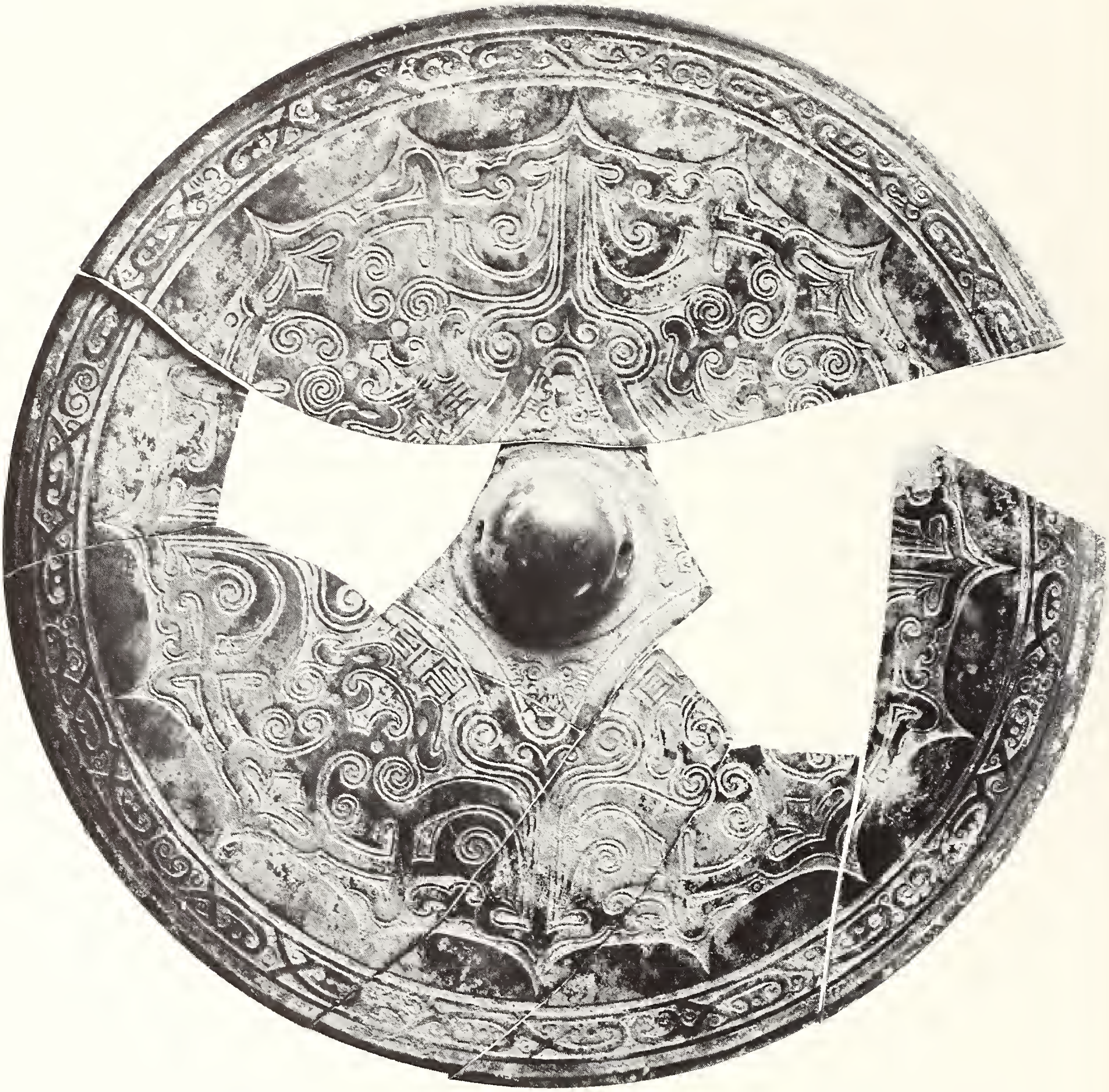

Fig. 1.—Mirror #1, black with patches of bright green; courtesy of the Royal Ontario Museum, Toronto, Canada. The Museum's catalogue card states: 960.234.49; 74 FAE 321; Con #689/197; Mirror, bronze, round, flat with patches of bright green patina. Hemispherical central knob, square central band with incurving sides, small animal masks inside each corner, main field decorated with four dissolved animal masks and 5 characters of what must have been an 8-character inscription. The whole is surrounded by one inward-facing scallop band and a scroll-pattern border. The Dr. James M. Menzies Collection. Broken in 8 pieces with 3 pieces missing. Late Han. Diameter $6\frac{3}{8}''$ (15.7 cm.)

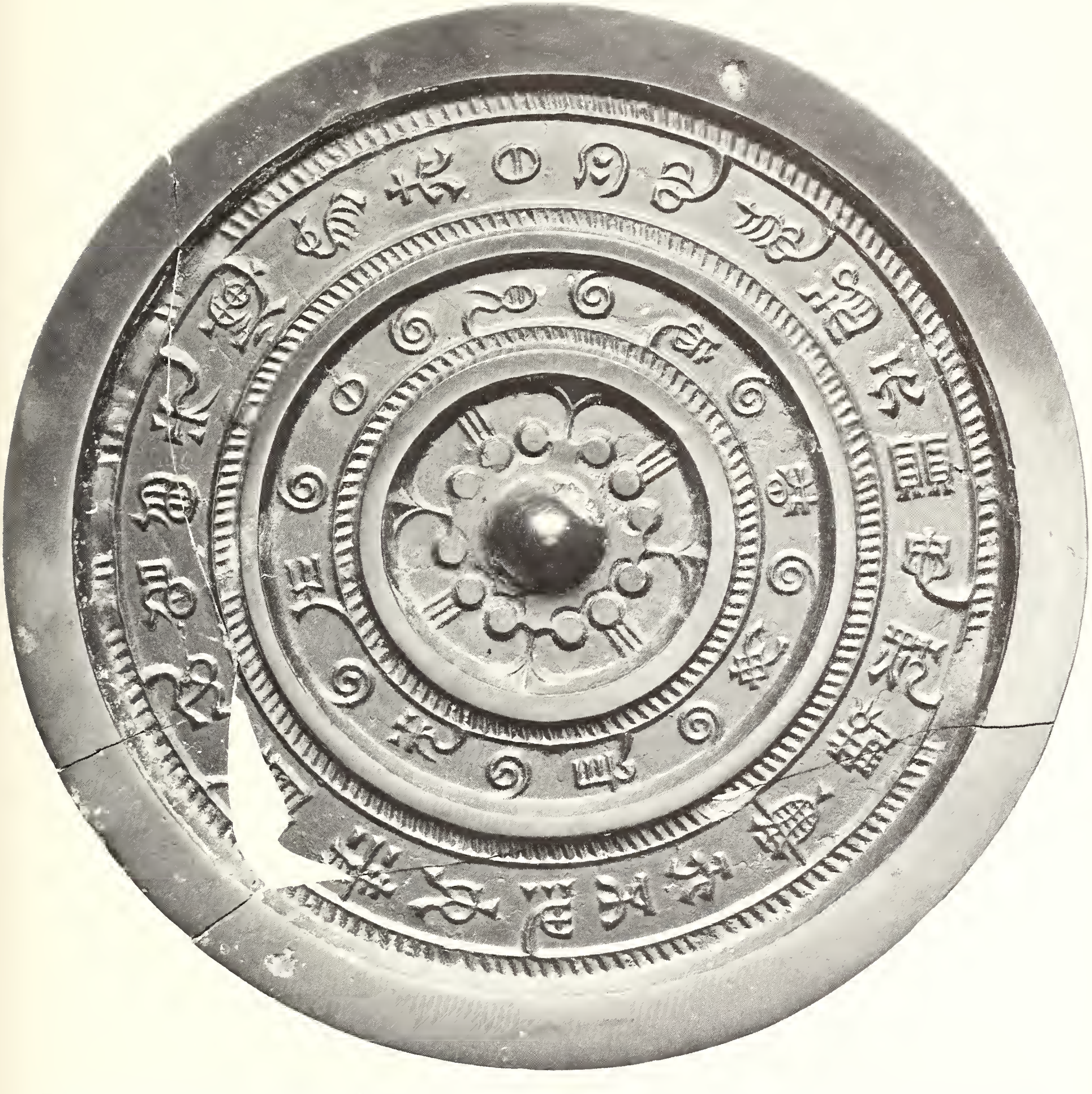

FIG. 2.—Mirror #4, black; courtesy of the Royal Ontario Museum. The Museum's catalogue card states: 960.234.41; 74 FAE 312; Con #689/195; Mirror, bronze, round with hemispherical knob, surrounded by 12 small circles in relief, enclosed by a broad flattened band in relief. Main decoration in a series of bands, first a band of closely spaced diagonal lines, surrounded by an inscription on a plain ground, a broad flattened band in relief, enclosed by a band of raised closely-spaced diagonal lines, a second inscription, surrounded by another band of raised closely spaced diagonal lines, an unturned flattened rim. The Menzies Collection (Estate of Dr. James Menzies). Broken in 5 pieces. Chinese, Han Dynasty. Diameter $6\frac{1}{8}''$ (15.4 cm).

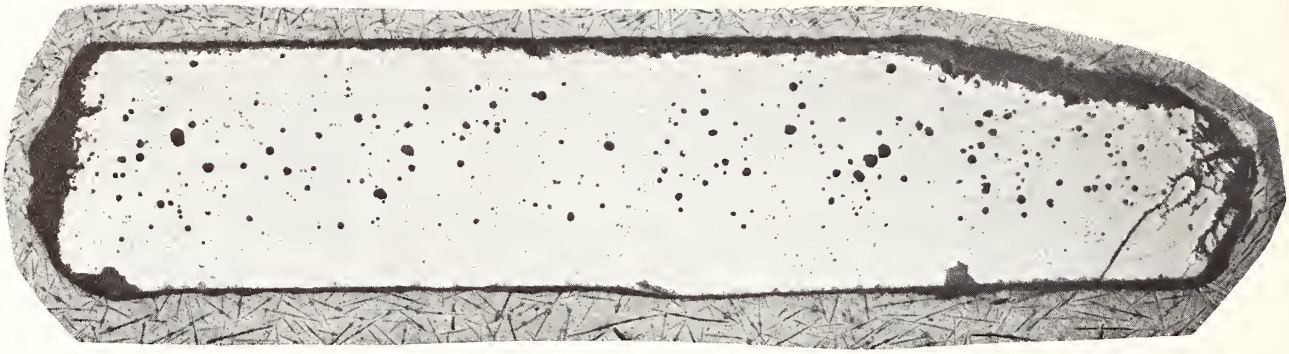

Fig. 3.—Cross section of Mirror #4; mounted in Wood's metal; ×7, bright field, unetched. The section shows the mirror face at bottom and the rim of the back at top; the rim slopes off at the right to the decorated area.

Microscopic studies. Figure 3 shows the fragment from Mirror #4 in full cross section. The fragment, mounted in Wood's metal, is shown in the polished but unetched condition. The as-cast structure and the near-spherical lead particles are clearly discernible. The black surface layer is of uneven thickness. The series of cracks in the narrower side of the fragment are of particular interest. One sees them—usually to a lesser extent—in cross sections of many black mirror fragments. The inside surfaces of the cracks show the same microstructural features as the material below the external surfaces of the mirrors.

Details of a smaller crack are illustrated in Figure 4, in which the external surface is at the top edge of the picture with the crack going at right angles to it into the mirror. It should be stressed that the lead-rich particles (which can be lead or lead-tin eutectic) are always spherical or near-spherical. We never saw evidence of liquation of lead or its appearance in interdendritic spaces, nor did we ever see structures that would indicate working or heat-treating of the bronze.

The metal itself exhibits the typical structure of a high-tin bronze with an α and $(\alpha + \delta)$ eutectoid phase as well as a fair number of inclusions. As evident in Figure 3, the large inclusions tend to segregate towards the center of the mirror, while the small ones (some of them sulfides) are evenly distributed throughout the matrix.

Our microscopic examination showed that

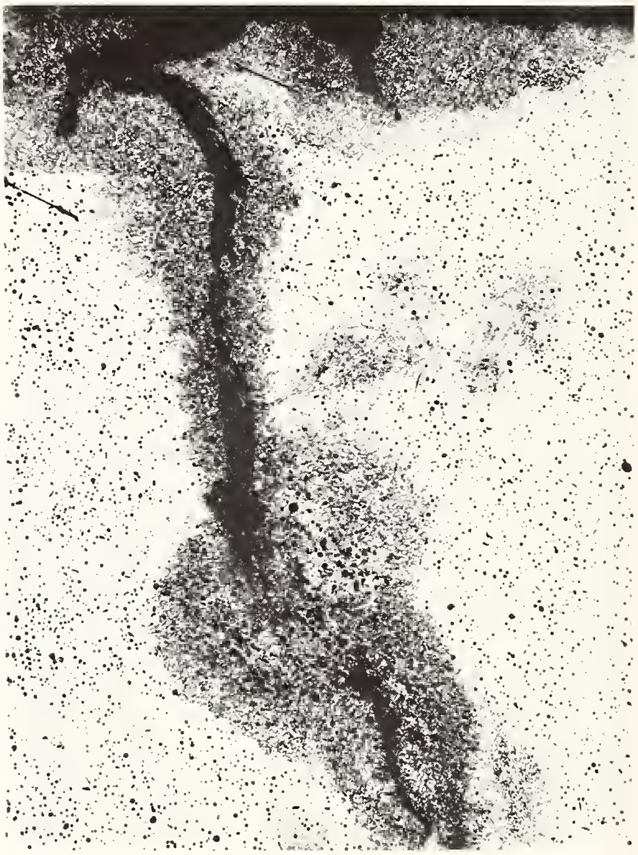

Fig. 4.—Mirror #4; detail of a crack normal to the surface; ×64, bright field, unetched.

there are three significant regions within the black mirrors—all clearly evident in cross section (fig. 5). The very top surface is a non-metallic layer that appears white or light green in bright-field reflected polarized light. This very thin surface layer merges smoothly and without discontinuity or interface into a band of a modified alloy. In this "altered zone", the α-phase of the original bronze is replaced by a consituent of a different chemical composition, while retaining the original morphology and the original space. It is replacement by volume rather than stoichiometrically. This three-layered structure has been seen by both authors on many samples of dark, shiny objects, both weapons and mirrors.[16]

As the distance from the surface increases, the altered zone gradually turns into the basic alloy. Under higher magnification the *gradual* nature of the transition from the altered zone to the basic alloy is strikingly evident.

The area shown in Figure 5 is located on the back of mirror #4. Effects of "contouring" are usually more pronounced on the decorated back than on the face. The way in which the altered zone follows the contours of the surface layer is quite characteristic and can be seen on many cross sections.

Etching experiments. After the three characteristic regions within the mirror were defined, various etchants were used to study the details of their structures. Ammonium peroxide, potassium dichromate, dilute ferric chloride and Villela's etch were employed. When, later in the study, sulfur prints were used to study the distribution of sulfur compounds within the bronze, the preparation of the sulfur prints produced an additional etching process as shown in Figure 6.[17]

In all cases the etchants were applied to a freshly polished surface of mirror #4, the largest sample at our disposal. None attacked the outermost, non-metallic layer in any discernible way. The effect of the etchants on the altered zone and the basic alloy can be summarized as follows.

Ammonium peroxide revealed the structure of the basic alloy and brought out the particles in the bronze, but it gave only a slight brownish tint to the altered zone.

Potassium dichromate attacked the bronze but only tarnished the altered zone. This led eventually to a noticeable difference in height, with the altered zone and the inclusions in the bronze standing up above the alloy surface.

Ferric chloride diminished the contrast between the alloy and the altered layer; the gradual transition between the two became even more gradual. Parts of the altered layer that were close to the external mirror surface appeared slate grey.

Villela's etch served mainly to bring out inclusions in the matrix and revealed the details of their structure. It did not selectively attack the altered layer.

Electron microprobe studies. A Norelco AMR/3 Electron Microprobe was used to relate chemical composition to the microstructural features.[18] It was operated at 30–40 kV with

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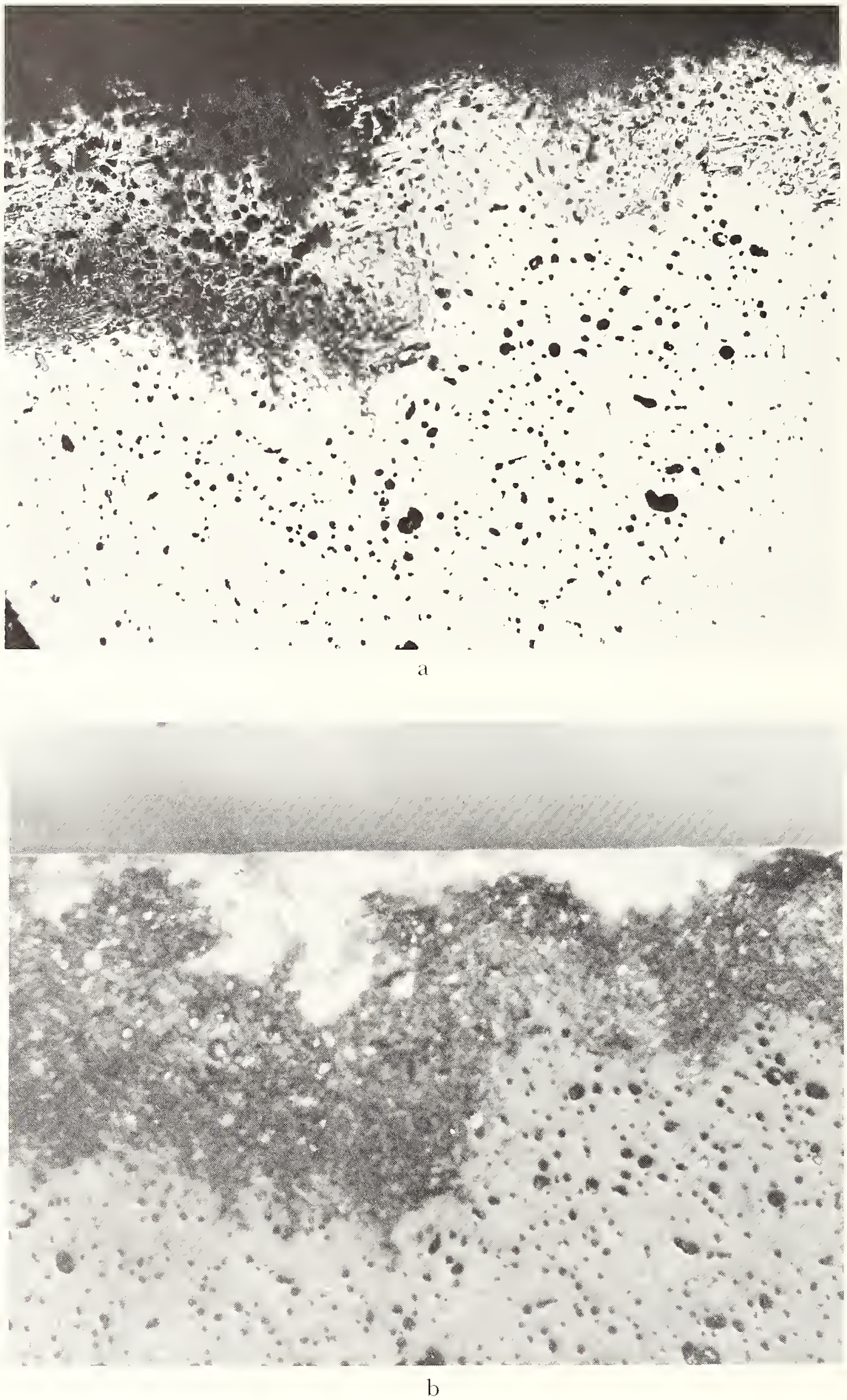
[16] W. T. Chase, "What is the Smooth Lustrous Black Surface on Ancient Bronze Mirrors?", *Corrosion and Metal Artifacts—a Dialogue Between Conservators and Archaeologists and Corrosion Scientists*, NBS Special Publication 479, ed. Brown, Burnett, Chase, Goodway, Kruger, Pourbaix, (U.S. Dept. of Commerce, Washington, D.C. 1977); Structured Discussion Question 1, Figures Q-1-6 to Q-1-10, pp. 195–196.

[17] George L. Kehl, *Principles of Metallographic Laboratory Practice*, (McGraw-Hill, New York, 1949).

[18] LaVerne S. Birks, *Electron Probe Microanalysis*, (Vol. 17 of the Chemical Analysis Series, Wiley-Interscience, New York, 1971).



a

b

FIG. 5.—*a*. Mirror #4, detail of the surface, showing, from the top: the glassy layer, the altered zone, and the body metal; ×187, bright field, unetched. *b*. Same as in *a*., in reflected polarized light.

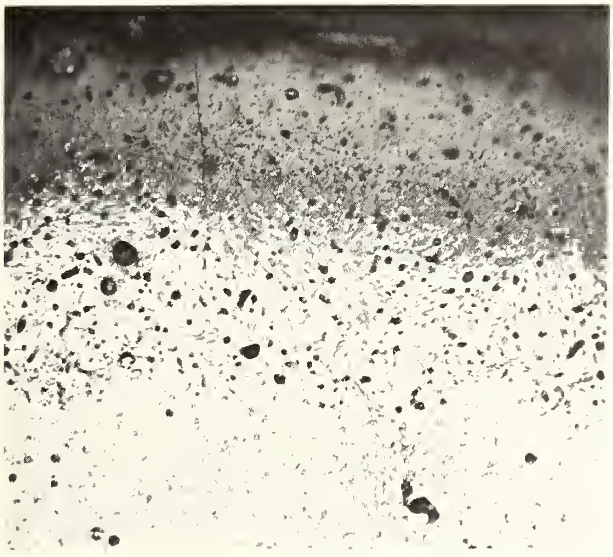


Fig. 6.—Mirror #1, detail showing the surface (glassy) layer and the altered zone; ×258, bright field, etched for sulfur print.

approximately 5.5 mA beam current. The electron beam could be focussed to ca. 3 μm diameter, but because of the coarseness of the structure, a 10 μm beam was usually employed. Sample surface observations were made at magnifications up to ×60 in polarized light. The 6° take-off angle of the instrument imposed fairly stringent requirements as to surface flatness; detection sensitivity of the flow-proportional counter and resolution of two bent-crystal spectrometers were excellent.

Elemental beam scans for Cu, Sn, and Fe on mirror fragment #4 are shown in Figure 7. The beam path was approximately normal to the surface and the sample was driven at a rate of 125 μm/min from one side of the mirror cross section to the other.

These traces illustrate the most distinctive characteristic of the black mirrors: the

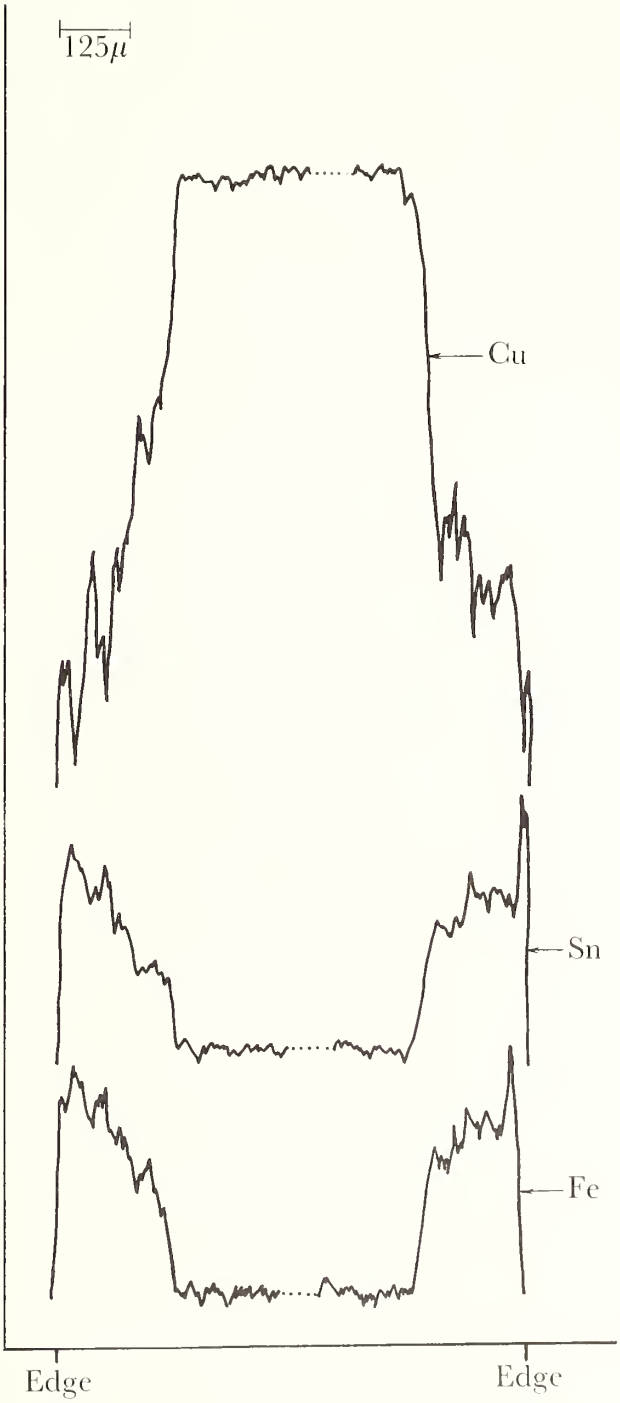


Fig. 7.—Composite of electron microprobe traces showing the composition of copper, tin and iron against a distance across a section of mirror #4. The heights of the traces are proportional to the CuKα_1, SnLα_1, and FeKα_1 intensities. The altered zone and glassy surface are seen to have more tin and iron and less copper than the body metal.

surface region—comprising both the non-metallic layer and the "altered zone"—is of a chemical composition distinctly different from that of the bulk metal. The thickness of this region can vary (thickness range approximately 200–500 μm), but the compositional pattern is always the same: copper, which comprises 70–75% of the bulk alloy, decreases to around 40% in the surface region. Tin, on the other hand, increases from about 25% in the bulk to about 40% on the surface. One finds substantial amounts of iron as well as silicon in the surface region. Iron occurs in the bulk alloy only as an impurity at levels of 1% or less, while silicon can hardly be detected at all in the bulk metal at the center of the mirror.

We have scanned ten fragments of different mirrors, each in several places on a cross section, and have consistently found the same or very similar compositional patterns: the appearance of Fe and Si, the decrease in Cu and the increase in Sn in the surface region.

A representative slower scan, recording two elements simultaneously, is reproduced in Figure 8. It shows the high concentration of Si in the very top surface, i.e., the non-metallic layer. In the altered layer the Si content is still high, but it drops to below 0.05% in the alloy proper. The Sn content, on the other hand, is more or less uniformly elevated in the whole surface region. Two experimental details should be noted: first, because of the lower concentrations present, the silicon Kα line is much more highly amplified resulting in larger apparent fluctuations of the recorded intensities. Second, the tin trace is offset the equivalent of 11 μm to the right to avoid overlapping.

The distribution of Fe in the surface region follows quite closely that of Sn. We found clear evidence of Fe in the inside layers of the cracks—such as the one in Figure 4. One of the authors (WTC) has previously published electron microbeam probe pictures of Sn, Fe, and Si concentrations on the cross section of a similar mirror from the Plumer Collection, which confirm the findings above.[19]

Mirror fragments were also placed into the microprobe with the black mirror surface in the plane of the sample, i.e., with the electrons impinging on the black surface. The top surface of the mirror was non-metallic and electrically strongly insulating. The complete lack of surface conductivity was also demonstrated by the fact that beam traces on the surface remained visible for weeks and did not fade. In order to determine the composition of the sample, all samples were subsequently coated with C, Al or Au. The films were thin enough to permit visual observation but adequate to avoid charge build-up.

Because of the references in the literature we carefully searched for mercury and for any organic compounds that could indicate the presence of lacquer. Organic material decomposes under the electron beam; the resulting contamination of the area is easily detected. Nothing of this nature was observed. We also failed to detect mercury in any part of the fragments.

As the experimental evidence accumulated, speculations arose as to the possible role of sulfur in the formation of the black surfaces. Sulfur was indeed present in most samples but after much probe work it became clear that the sulfur was associated with inclusions which were evenly distributed throughout the alloy. The inclusions frequently exhibited

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[19] Chase, "What is the Lustrous Black Surface . . ."

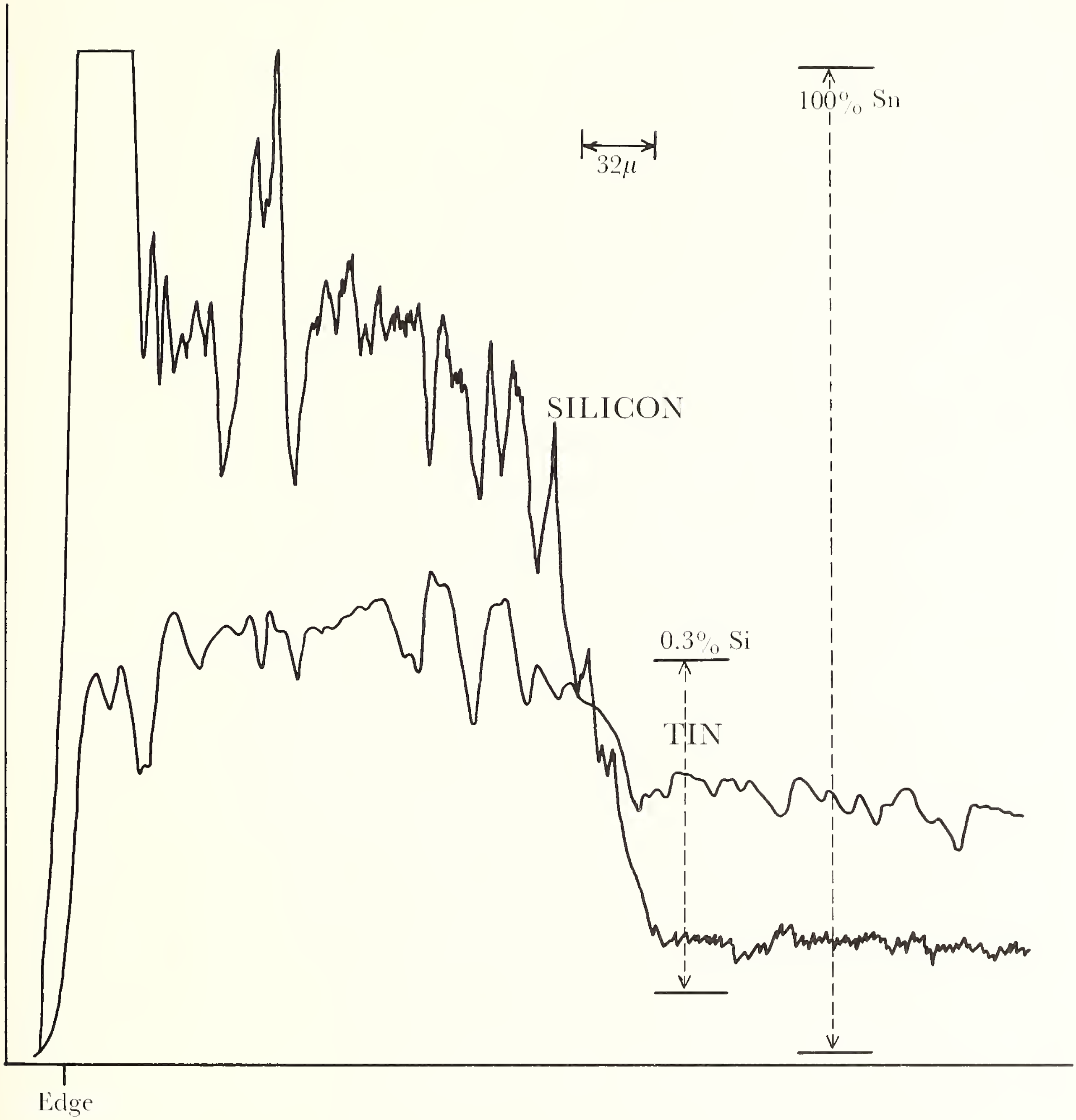

FIG. 8.—Electron microprobe traces showing the SnLα and SiKα intensities across the glassy surface and the altered zone of mirror #4. The glassy surface, ca. 30 μm thick, at left, is enriched in silicon. Silicon is present in the altered zone, and is present only as a trace (ca. 0.03%) in the body metal. The traces were made with two spectrometers simultaneously; the tin trace is slightly displaced to the right to prevent overlapping.

fluorescence under the electron beam. The distribution of sulfur was confirmed by sulfur prints taken on several cross sections.

X-ray fluorescence analysis. All samples at our disposal were analyzed by X-ray fluorescence. Heavier elements were analyzed using a LiF crystal; the lighter elements were detected by a flow counter from the reflection off an ADP or EDDT crystal. A Siemens SRS was in every case operated with an evacuated path. The overall compositional pattern discussed above was confirmed, and impurities such as S, Zn, Co, Mn, Bi, Ag and As were detected (not all impurities in every mirror fragment). It is difficult to utilize this information since we could not assemble the corresponding data for non-black mirrors under the same conditions. Analyses reported in the literature are usually obtained from samples from which "corrosion products" were carefully excluded. This practice, more than anything else, must have prevented Gettens and Collins from detecting iron in the surface layers of the black mirrors.

X-ray diffraction studies. Considerable effort was expended to obtain information about the mirror's surface layer by means of X-ray or electron diffraction. The electron microprobe experiment had shown that the layer is non-conductive; optical microscopy had revealed it to be a white to light green, isotropic, glassy looking substance. Like all others who have studied black mirrors we found it difficult to remove pure fragments of this layer. The intimate interlinking between this region and the altered layer beneath makes it almost impossible to obtain a well-defined sample containing only the non-metallic constituent of the top layer. Even if one were to dissolve the bronze proper using electrolytic or other means, all other inclusions and products of internal corrosion would remain. Therefore, we chose three separate approaches: (1) The plain side of mirror fragment #4 was used directly as a sample in a diffractometer, employing Cr, Cu and Mo radiation. The sample was large enough and flat enough to allow a reasonably accurate recording of the diffraction patterns. (2) A few small surface fragments were dislodged. After slight grinding, they were used as samples in a Debye-Scherrer camera. (3) We also attempted to use the smaller mirror fragment as sample in a Guinier camera.

In the series (1) above, CrKα radiation, being the least penetrating of the X-rays used, gave only faint broad lines around the d-values of 5.16, 3.32, 3.97, 2.60 and 2.50 Å; in addition a few very weak but sharp lines appeared. These lines became stronger as the penetration depth of the radiation was increased by changing to CuKα and MoKα. These lines could be identified as diffraction patterns from the bronze proper. No new lines attributable to the surface layer appeared on the patterns obtained with Mo radiation. The Guinier camera experiments yielded very similar results.

Over the years we analyzed a dozen different powder diffraction samples removed from the top layers of black mirrors. In most of them, we found patterns similar to the one from mirror #1, shown in Table 1: this was a fairly large composite sample of the surface layer containing material from the altered zone as well.

Regarding the identification of these patterns, it is, in general, often difficult to identify certain oxides unambiguously by X-ray diffraction alone. The crystal structure of some metal oxides can be very similar, since the large oxygen atoms mainly determine the packing. Solid solubility of oxides in each other can also be substantial. To

TABLE 1

X-ray Powder Diffraction Pattern Measurements from the Surface Layer of Mirror # 1, Compared with Various Oxides.

Black coating #947, 33A #947, 33b		SiO_2 5–0494		SnO_2 21–1250		CuO 5–0661		Cu_2O 5–0667		Fe_2O_3 13–534		Fe_3O_4 19–629	
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
10.13	1												
8.24	1												
7.17	1												
6.34	1											4.85	8
4.46	2												
4.25	8	4.26	35										
4.03	1												
3.92	1												
3.79	1												
3.67	1									3.66	25		
3.49	1												
3.34	10	3.34	100										
3.19	4												
3.03	4							3.02	9				
												2.97	30
						2.75	12			2.69	100		
				2.64	80	2.53	49						
2.55	1					2.52	100			2.51	50	2.53	100
2.45	5	2.45	12					2.46	100			2.42	8
				2.37	25	2.32	96						
2.28	5	2.28	12	2.31	6	2.31	30			2.28	2		
2.24	2	2.23	6							2.20	30		
2.13	5	2.12	9	2.12	2			2.13	37	2.07	2	2.10	20
1.98	3	1.98	6			1.96	3						
1.82	7	1.81	17			1.87	25			1.84	40		
		1.80	<1			1.78	2						
				1.76	65	1.71	8	1.74	1			1.72	10
1.67	2	1.67	7	1.67	18					1.69	60		
1.66	1	1.65	3							1.63	4		
		1.60	<1	1.59	8	1.58	14			1.60	16	1.62	30
1.54	7	1.54	15										
1.50	1			1.50	14	1.50	20	1.51	27	1.48	35	1.49	40
1.45	2	1.45	3	1.44	18	1.42	12			1.45	35		
		1.41	<1	1.41	16	1.41	15					1.42	2
1.38	6	1.38	7	1.38	19								
1.37	7	1.37	11							1.34	4		
				1.32	8					1.31	20	1.33	4
1.29	3	1.28	3			1.30	7	1.28	17			1.28	10
1.26	4	1.25	4			1.265	6			1.258	8	1.246	4
1.23	2	1.22	2	1.21	12	1.262	7	1.23	4	1.226	2		
{1.20	5}	1.199	5							1.213	4	1.212	2
{1.20	5}	1.19	2			1.196	2						
1.18	4	1.183	4	1.18	4					1.189	8		
						1.1697	5						
						1.158	3			1.162	10		
		1.15	2	1.15	8	1.156	4						
										1.141	12	1.122	4
		etc.		etc.		etc.		etc.		etc.		etc.	

Note: Except for the mirror black coating, all data is from the JCPDS Powder Diffraction File; card numbers shown under the compounds.

illustrate the problem, we have included in Table 1 diffraction patterns of some relevant oxides. Difficulties of identification are compounded by the fact that in archaeological samples we cannot expect pure oxides.

It appears, therefore, not possible to deduce from the diffraction data the structure of the mirrors' top surface layer, which may, in fact, be essentially amorphous; we have frequently seen quite narrow and sharp α-SiO_2 lines in diffraction samples of mirror surface fragments—through often weaker than in the example given here. This may indicate local recrystallization in the amorphous layer.

The diffraction data *do* permit us to rule out several previously suggested compositions: the surface layer does not contain tenorite, nor any new Cu-base alloy phase; SnO_2 is virtually ruled out as a surface constituent, and so is Fe_2O_3 or Fe_3O_4.

The evidence clearly indicates that the surface material is a glassy, amorphous silicate containing Sn, Fe, Pb and some Cu. Gettens' refractive index determination ($n = 1.78$–1.81)[20] also suggests the possibility of a heavy-metal glass.[21]

Hardness measurements. Figure 9 shows the results of hardness measurements on the cross section of Fragment #4, given in Vickers diamond pyramid hardness numbers. Because of the coarse and heterogeneous alloy, the actual measurements were carried out on a Tukon hardness tester with a spherical indentor and a load of 100g (this procedure was adapted to minimize the effects of local microstructure variations). The radius of the indentation was converted to VHN by using the formula: $VHN = Cp/r^2$ with the radius of the identations, r, in mm, $p = 100$ g and $C = 5.520$. The area tested was adjacent to the one shown in Figure 5. Though the local hardness shows variations, as indicated in Figure 9, an overall trend is clearly discernible—the very top layer is hardest and the altered layer, though harder than the basic bronze, is not as hard as the outside surface. A second set of measurements on the same sample, but in a different location, yielded an average hardness number of 373 (from four different indentations) for the top layer and average hardness of 353 (five separate indentations) for the altered layers. The hardness data illuminate again the process of a uniform and stable mineralization.

The average hardness derived from the alloy metal shown here (341) agrees in magnitude with the hardness shown for a chill-cast 25% tin bronze (ca. 300 Brinnell hardness).[22]

Density measurements. Early in our study we determined the density of several fragments as part of our overall investigation. Density measurements, which are totally non-destructive, can provide useful diagnostic information. Unusually low densities may indicate mineralization, porosity, or internal corrosion; high densities can point to metallic inclusions, etc. The method described by Caley[23] yielded densities between 8.75 and

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[20] Gettens, "Tin-oxide Patina . . .", p. 22.

[21] In interpreting the X-ray diffraction data, one should also consider that compounds from glass devitrification may also be present. For instance, see J. Carbo Nover and J. Williamson, "The Crystallization and Decomposition of SnO–SiO_2 Glasses," *Physics and Chemistry of Glasses*, vol. 8, no. 4 (August, 1957), pp. 164–168, where a glass of composition 46% SnO, 53% SiO_2 and $n = 1.652$ is cited as yielding an SnO–SiO_2 devitrification product.

[22] D. Hanson and W. T. Pell-Walpole, *Chill-cast Tin Bronzes* (Edward Arnold & Company, London, 1951), p. 243, Figure 151.

[23] Earle R. Caley, *The Analysis of Ancient Metals* (Pergamon Press, New York, 1964), p. 44ff.

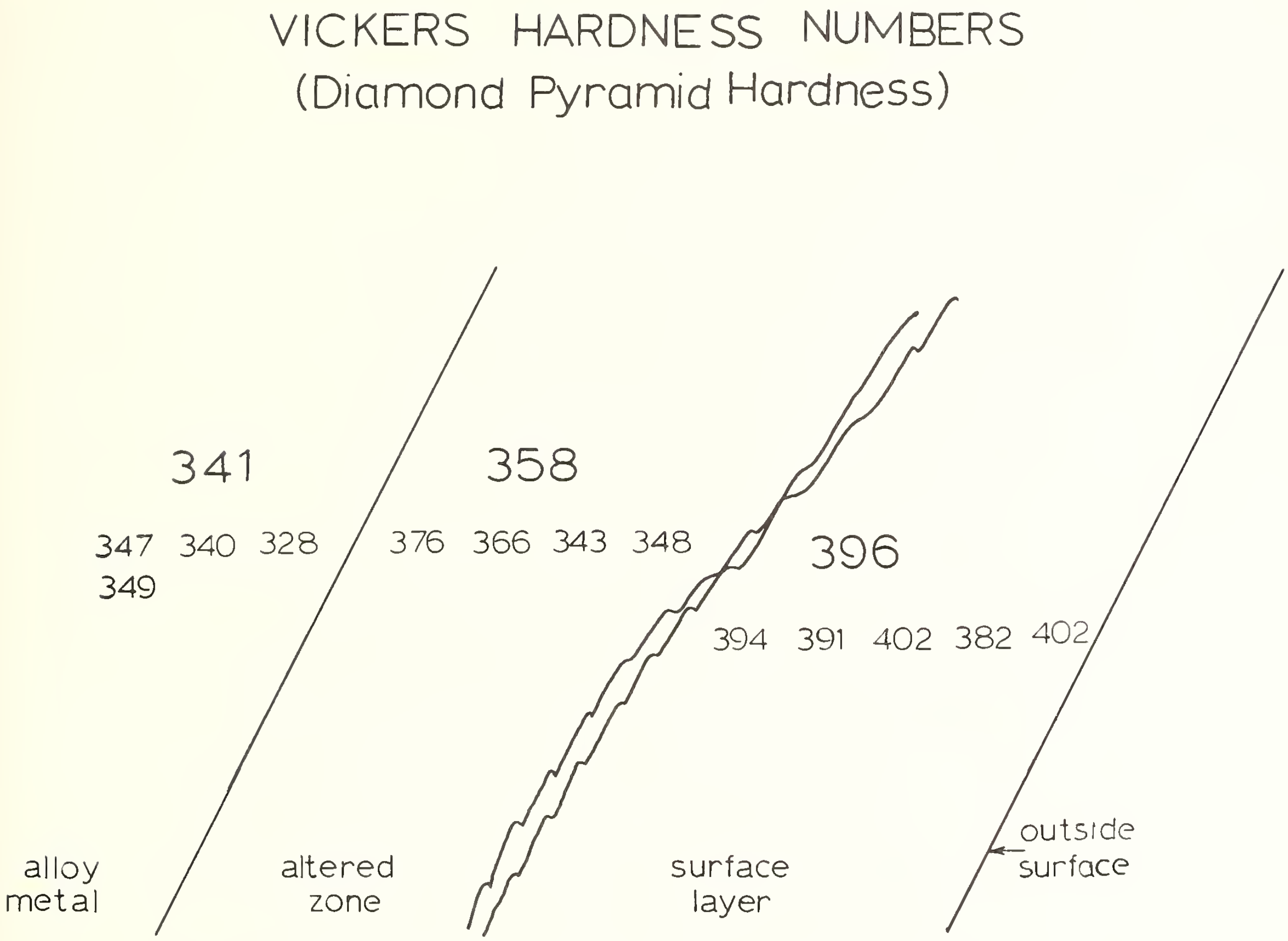

Fig. 9.—Hardness measurements on the surface layers of a cross section of mirror #4.

8.78 kg/m^3. Bronzes of the composition of Chinese mirrors are rarely used in modern times; their extreme hardness and brittleness render them difficult to fabricate by industrial processing techniques. For this reason, it is difficult to find density figures with which to compare the density values from our fragments. A modern SAE 63 bronze (87% Cu—10% Sn—1% Pb—2% Zn) has a density of 8.8 kg/m^3, SAE 64 bronze (80% Cu—10% Sn—10% Pb), a density of 8.95 kg/m^3 [24]. A 25% tin bronze can be seen to have a density of 8.92 kg/m^3 from Hanson and Pell-Walpole's data, which have been redrafted for comparison by Chase and Ziebold[25]. The

[24] American Society for Metals, *Metals Handbook*, vol. 1, 8th Edition (ASM, Metal Park, Ohio, 1961) pp. 1038–1039.

[25] *Chill-cast Tin Bronzes*, p. 253, Figure 167; W. T. Chase and T. O. Ziebold, "Representations of Ancient Chinese Bronze Compositions," Chapter 18, pp. 293–334, in *Archaeological Chemistry* II, ed. Giles Carter (Advances in Chemistry Series no. 171, American Chemical Society, Washington, D.C., 1978).

density range of our fragments is slightly lower than that of the modern bronzes; considering the possible inclusion of oxide and corrosion products in our samples, the data agree quite well.

Summary of the technical evidence. The experimental results from the two cases above are consistent with those from approximately forty other black mirrors examined by the authors, both in Toronto and Washington. About twenty mirrors were examined in detail, and another twenty less thoroughly examined. From all this information, a picture of the "prototypical black mirror" emerges: it is made of a high-tin bronze containing ca. 70% Cu, 25% Sn, and 5% Pb. This alloy is silver-white, melts at around 800°C and is hard and brittle. The prototypical mirror was cast and cooled in a manner no different from other Chinese bronzes: casting sprues, flash, etc. were removed and relief decoration (probably) lightly finished; the remainder of the mirror was given a high polish by the use of abrasives. No working or annealing was performed.

After polishing, the surface of the mirror was in some manner "sealed" and rendered inert to environmental attacks. The "sealing" process gave the mirrors their non-metallic surface, which appears to be an amorphous silicate or mixed oxide containing SiO_2. Below this non-metallic layer, the original bronze structure is significantly altered. The α-phase of an alloy is replaced—isomorphically and by volume—by an iron-containing compound, while the δ-phase remains. Thus, the surface region, both the shiny surface layer and the altered zone beneath, is enriched in tin and depleted of copper. It also contains silicon and iron as major constituents; in the body of the mirror silicon and iron occur only in trace quantities. The surface region is somewhat harder than the mirror itself, and the entire object is very dense and compact throughout. The transitions from the non-metallic layer to the altered zone and from the altered zone to the bronze proper are gradual, with neither interface nor porosity apparent. The non-metallic surface layer is lightly colored and transparent; the black (or brown or green) coloration appears to come from the altered zone seen through the transparent surface.

THE SURFACE LAYER—NATURAL OR ARTIFICIAL?

Approaches to the problem. Was the black surface intentionally produced? To answer this question conclusively, we must examine other dark, shiny bronzes which were (probably) not intentionally patinated. Then we must determine the limits of time and place of the production of the black surface, scan the historical evidence for black mirrors, and compare other metal objects with intentional surface treatments. If the black, shiny surfaces were produced by a craft technique, then this technique would have a beginning and may have a height and a decline; there would be a time before which black mirrors were not produced. We should find a geographical distribution according to production; variations in surface treatment, if intentional, will not be dependent on local environmental (corrosion) conditions. Let us see what evidence there is before attempting to decide if the black of the mirrors is intentional.

Naturally corroded dark, shiny bronzes. Can Chinese bronzes acquire a black surface solely through burial? Dark, shiny surfaces appear on a number of ceremonial vessels in the Freer Gallery.[26] On *p'ou* 13.30, a shiny dark-green tin oxide corrosion product pseudomorphically replaces the metal. The δ-phase can be seen to have corroded first. On *tsun* 25.2, a similar but deeper pseudomorphic replacement has occurred. The tin oxide patina on this *tsun* is very dark olive-green, almost black.

In both cases, corrosion has proceeded with the δ-phase first, leaving islands of uncorroded α-phase. This is the normal order of corrosion for Chinese bronzes. We have no reason to think that these two bronzes were artificially patinated. No glassy layer shows on the surface, and the corrosion product is the usual stained tin oxide.

Turning to excavated material, the *fang yi* inscribed for *Jih Chi*, excavated in 1963 at Fu-feng, Shensi, has a fine shiny black patina spotted with green, matte areas.[27] A bail-handled *yu* dating from the Shang dynasty and excavated at Ninghsiang, Hunan, also has a shiny black patina.[28]

Many more examples of archaeologically excavated bronzes with shiny black or dark green surfaces could be cited. While we have no metallographic sections, as yet, from any of these, it seems likely that the corrosion may be the usual pseudomorphic replacement of the metal with tin oxide, and that the corrosion has probably proceeded with the δ-phase first.

Bronzes with shiny dark surfaces have been recovered from the central loess area of China (Shensi, Shansi and Honan provinces) and from other areas as well, as the *yu* from Hunan, above, demonstrates. It seems likely to us that dark patinas on early bronzes are simply the result of burial. Corrosion on ancient Chinese bronzes usually begins with the loss of the δ-phase; initial removal of the α-phase may well be indicative of intentional patination.

Geographical and chronological limits of black mirrors. While sporadic examples of Shang mirrors had been adduced before,[29] the excavation of the tomb of Fu-hao at Yin-hsü, An-yang, in 1976 proved the existence of Shang bronze mirrors beyond doubt.[30] Four mirrors were found, ranging in size from 12.5 to 7.1 cm in diameter. The front is almost flat, and the simple geometric designs on the back tally with those on other supposedly Shang mirrors. From the photographs in the excavation report, these mirrors do not appear to be black. The context has been dated to the reign of king Wu-ting of Shang by Chinese writers.

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[26] Rutherford J. Gettens, *The Freer Chinese Bronzes, Volume II, Technical Studies*, Smithsonian Institution Oriental Studies No. 7, (Freer Gallery of Art, Washington, D. C., 1969), p. 188, Figure 251 and Figure 253.

[27] William Watson, *The Genius of China*, an exhibition of archaeological finds of the People's Republic of China, held at the Royal Academy, London . . . (London, 1973), p. 93 and color plate 93; Anon., *The Chinese Exhibition*, an illustrated handlist of the exhibition of archaeological finds of the People's Republic of China, (National Gallery of Art, Washington, D.C., 1975), color plate 95.

[28] Anon., *New Archaeological Finds in China*, discoveries during the Cultural Revolution (Second edition revised, Peking, 1973), color plate 2.

[29] Doris Dohrenwend, "The Early Chinese Mirror," *Artibus Asiae*, vol. 27, nos. 1 and 2 (1964), pp. 79–98; William Watson, *Ancient Chinese Bronzes* (Faber and Faber, London, 1962), p. 81ff; Sueji Umehara, "Ancient Mirrors of the Yin and Chou Dynasties (Chūgoku in-shu no Kokyō)," *Shirin*, no. 4 (1959), pp. 467–480.

[30] The An-yang Archaeological Team of the Institute of Archaeology, Chinese Academy of Social Science, "Excavation of Tomb no. 5 at Yin-shü in An-yang," *Kaogu Xuebao*, no. 47 (1977, no. 2), pp. 57–98.

The next securely dated group of mirrors comes from the cemetery of the state of Kuo at Shang-ts'un-ling.[31] Kuo was a small state annexed by Chin in 655 B.C.; the cemetery dates from the late Western Chou or early Period of the Spring and Autumn Annals. Two of the mirrors are plain and look like normally corroded bronze (nos. 1650:1.1 and 1650:1.2, diameters 5.9 and 6.4 cm respectively). The third has a design of four roughly drawn animals in relief, and a doubled-ring handle (no. 1612:65, diameter 6.7 cm). As shown in Plate 40 of the excavation report, this mirror looks quite black and shiny. Another object, very probably a mirror, was found in tomb 1052.[32] It shows a back decorated in Western Chou style, which again appears to be black. Two very early swords were also found at Shang-ts'un-ling.[33]

To sum up: while two of the Shang-ts'un-ling mirrors may have the black surface, two probably do not. No analyses or sections have been published from these objects. It is impossible to say whether this black has simply come from burial or is an example of the artificial "mirror black" coating.

In contrast to Western Chou, in Eastern Chou times the number of mirrors vastly increases. Barnard lists 124 mirrors of Warring States date; the total number of mirrors excavated from controlled conditions before 1966 is over a thousand! Barnard also alludes to the need for a re-examination of the chronology of mirrors with reference to the recently excavated material, and he notes the connection of mirrors with the Ch'u state.[34]

While it is true that mirrors are more frequently found in excavations in the Ch'u state areas than elsewhere, the earliest mirrors yet excavated come from Yin-hsü (An-yang) and from Shang-ts'un-ling in the state of Kuo. Dohrenwend, while leaving the question of the Scythian origins of Chinese mirrors open, makes a good case for cross-cultural influence between the northern nomads and the Chinese in determining mirror design,[35] as does Lubo-Lesnichenko.[36] Parallels could be drawn between mirrors and weapons; one especially fine knife of the Scythian type occurs in the Shang tomb of Fu-hao with the early mirrors.[37]

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[31] Institute of Archaeology, Academia Sinica, ed., *The Cemetery of the State of Kuo at Shang Ts'un Ling* (Shang Ts'un Ling Kuo-kuo Mu-ti), Archaeological Excavations at the Yellow River Reservoirs Report No. 3, (Academia Sinica, Peking, 1959), p. 77, figures 20 and 21, and plates 23 and 40. Dohrenwend, "The Early Chinese Mirror."

[32] . . . *Shang Ts'un Ling*, Number 1052:56; plate 38, no. 13.

[33] . . . *Shang Ts'un Ling*, p. 84.

[34] "However, a general reappraisal of all investigations will probably be needed before long and it is essential that it should be made with the rapidly growing corpus of properly provenanced finds acting as a means of control. Most of the earliest mirrors reported (Map 10a) come from Late Ch'un-ch'iu sites near Ch'ang-sha, Chiang-ling, and Sung-tzu; there are a number of early Chan-kuo mirrors unearthed in these sites, too, and also in Ch'ang-te. Accordingly, Ch'u would seem to be the area of origin of the mirror. The rapid spread of this new artifact and its general popularity is well evidenced both in the distribution patterns of the chronological maps, and in the rather wide dispersal of site-areas with totals of 15 or more mirrors. Lo-yang has the largest number of mirrors excavated (305); three other site-areas have each reported 100 or more mirrors (3:31, 6:1, and 11:1). [Yu-hsien, Pai-sha-chen, Honan; Kuei-hsien, Yünnan; and Ch'ang-sha, Hunan, respectively.] Altogether somewhat over 1,295 mirrors are entered in the Table of Sites and Remains; the statistics are as follows: six mirrors of Ch'un-ch'iu date have been excavated from three site-areas, 124 of Chan-kuo date from 22 site-areas, and 542 of Eastern Han date from 93 site-areas. Although the average per site-area drops from Western Han to Eastern Han, the marked increase in site-areas with mirrors in the later period is, no doubt, the more significant feature." Noel Barnard and Satō Tamotsu, *Metallurgical Remains of Ancient China* (Nichiosha, Tokyo, 1975), pp. 128–131 and p. 163ff.

[35] "The Early Chinese Mirror," p. 96ff.

[36] E. I. Lubo-Lesnichenko, *Privoznye Zerkala Minusinskoi Koloviny*, Kultura Namodov Vostoka, Mamerialy I Issledovanie, (Akademia Nauk SSR, Glavnaya Redaktsiya Vostoehnoi Literatury, Moscow, 1975), pp. 159–165.

Dohrenwend states that the evolution of Chinese mirrors proceeded through both round and square types made of two plates of metal (so-called "double plate" or "openwork back" types) to the more common solid types which are well-known from the late Chou and Han periods. She places the origin of the double-plate types in Lo-yang or the more northern centers. It is interesting that in this context she mentions the Li-yü style and states that "this might now more accurately be called the Hou-ma style."[38]

Hou-ma is the best-preserved late Chou bronze foundry site which has yet come to light, and the first in which pattern-molds and pattern-stamps have been found. In fact, the production of bronzes and their decor in terms of pattern replication techniques[39] was carried out at Hou-ma in a mature form. Decor in two layers using pattern-stamping is clearly one of the determining factors in the appearance of late Chou Chinese mirrors.

> Once it was discovered that the effect of a superimposed design on a patterned background could be achieved by pressing the rim or the design stamp down harder upon the mold than the pattern stamp, the Huai mirror craft was technically prepared for any design that could be developed upon the former. This stage seems to have been reached with Karlgren's Cl, or in the sixth century B.C.[40]

This is precisely contemporary with the early phases at Hou-ma; a Hou-ma provenance would not be unlikely for the mirrors in Karlgren's A group, especially A2, with a main motif of interlaced dragons surrounded by a border of cowries, nor in the B group, with the sole decoration of monster masks.

None of the mirrors pictured by Dohrenwend in her Group I or II (double-plate mirrors ranging from 7th to 5th century B.C.), nor the mirrors pictured by Karlgren in Groups A and B (his earlier groups) have black patinas. It is only when we get into the slightly later groups whose decoration relates to the style of the Ch'u state that the typical mirror-black surfaces appear. It is interesting that the mirror Dohrenwend reproduces as Plate I, Figure 16 is a late double-plate type, the only double-plate mirror known from Ch'ang-sha, excavated in 1954 from Grave MO11 of the Warring States Period, "Face and decorated back are of different color metal, the former being bluish-black and the latter appearing greyish." This specimen, possibly an import from the north, might conceivably have been the impetus of mirror production in Ch'ang-sha.

Soon after the general introduction of mirrors in the 7th or 6th century B.C., they became a popular item for personal use and, therefore, for tomb burial. Many appear to be black and shiny, judging from the published photographs. One of the authors (WTC) saw some excavated examples in the People's Republic of China on a trip in 1973.

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[37] See above; also Max Loehr, *Chinese Bronze Age Weapons*, (University of Michigan: Ann Arbor, 1956).

[38] "The Early Chinese Mirror," p. 85.

[39] Barbara Keyser, "A Technical Study of Two Late Chou Chien," *Bulletin of the American Institute of Conservation*, vol. 13, no. 3 (1975) pp. 50–64, and "Decor Replication in Two Late Chou Bronze *Chien*," elsewhere in this volume.

[40] Doris Dohrenwend, "The Early Chinese Mirror," p. 98; Bernhard Karlgren, "Huai and Han," *Bulletin of the Museum of Far Eastern Antiquities, Stockholm*, no. 13 (1941); *idem*, "Some Pre-Han Mirrors", *Bulletin of the Museum of Far Eastern Antiquities*, no. 35 (1963), pp. 161–169.

A number of mirrors from the Ch'ang-sha excavations were then housed in the Study Museum of the Institute of Archaeology (Chinese Academy of Social Sciences) Peking; they are indeed black and shiny.

Of the mirrors excavated in Hunan, 79% are black; this is a slightly greater proportion than those from Lo-yang (71%) and much greater than those found in Szechuan (39%).[41] It should, however, be pointed out that about 30% of the mirrors counted for Hunan are Chou and Early Han types; only 6% of those for Lo-yang were of this period; more are Han Dynasty mirrors.

Of three mirrors from the Man-ch'eng tombs of Liu Sheng, Prince of Ch'ung-shan, and his wife (Former Han Dynasty), two were shiny and black; one (the smallest of the group) was not.[42] The conditions in the Man-ch'eng tombs were quite dry and favorable for the preservation of metal objects.

As stated above, the entire history of Chinese mirrors deserves another more careful look on the basis of the archaeological evidence, with an eye to intentional surface treatments. While this brief survey can only serve to whet one's appetite for a really definitive study, one can draw some clear inferences concerning the black mirrors.

(1) Both black, shiny mirrors and mirrors without the black surface occur in archaeological excavations of Chou and Han sites in China. Sometimes, in fact, both have been excavated from the same context.

(2) The black surface is seen on many mirrors excavated from the ancient domain of Ch'u. It seems to be more common on pre-Han southern mirrors, and to spread throughout China on Han mirrors. Whether this impression will be confirmed by the archaeological evidence remains to be rigorously tested.

(3) Black mirrors are seen dating from at least as early as the beginning of the Warring States period, and they continue into the Han dynasty.

(4) Mirrors were easily transported over great distances and were much in demand. The mirrors from the Man-ch'eng tombs comprise one type each from Karlgren's categories F, J, and K; F is a category he assigns to the Shou-chou region, while J and K are assigned to the Lo-yang region. All three categories date from the 2nd century B.C.[43] The only unusual features of these mirrors are their size and their northern provenance, 400–500 miles from the putative places of manufacture. A fragment of a typical TLV mirror, apparently with the black surface, was found in Pazyryk (along with Sarmatian silver and unornamented bronze mirrors) some 1650 miles from Lo-yang.[44]

The hypothesis of an intentional surface blackening technique, first widely used in

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[41] Hunan Provincial Museum, *Hunan Ch'u-t'u T'ung-ching t'u-lu* (Bronze mirrors excavated from Hunan), (Wen Wu Press, Peking, 1960); count 119 (79%) black, shiny, 32 (21%) not; Lo-yang Shih wen-wu-kuan-li; wei-yuan-hui, *Lo-yang ch'u-t'u ku-ching* (Wen Wu Press: Peking, 1959), count 74 (71%) black, shiny, 30 (29%) not; Szechuan Provincial Museum, *Szechwan Sheng ch'u-t'u-tuang-ching* (Wen Wu Press: Peking, 1960), count 29 (39%) black, shiny, 45 (60%) not; see also Karlgren, "Some Pre-Han Mirrors"; Jan Fontein and Tung Wu, *Unearthing China's Past.* (Boston Museum of Fine Arts: Boston, 1973), p. 79 and 80.

[42] Anon., "A Report on the Excavations of the Han Tombs at Man-Ch'eng (*Man Ch'eng Han mu Fa Chüeh Chi Yao*)," *Kaogu*, no. 1 (1972) pp. 8–18; Chase, "What is the Smooth Lustrous Black Surface . . .," p. 185, Figure Q-1-1A and color plate O.

[43] Karlgren, "Huai and Han."

[44] Sergei I. Rudenko, *Frozen Tombs of Siberia: The Pazyryk Burials of Iron Age Horsemen*, translated by M. W. Thompson (University of California Press: Berkeley and Los Angeles, 1970) plate 70.

Ch'u and spreading to all China after the Ch'in unification and the beginning of Han, is not contradicted by the conclusions above. The evidence, especially that of differently colored mirrors in the Man-ch'eng tombs and the black mirror in Pazyryk, where corrosion conditions would have been vastly different than in central or south China, weighs against the black being a natural corrosion product.

THE ORIGINAL COLOR OF THE MIRRORS

Material evidence. To determine the original color of the mirrors, we must bring to bear all the material, literary, and pictorial evidence available. The material evidence is described above. The mirrors (and some of the weapons) are made from a high-tin bronze (ca. 70% Cu, 25% Sn, 5% Pb). This alloy is hard and silvery white when cast and polished. It makes a fine mirror.

The present color as seen on the black mirrors is due to the attenuated reflection of light from a black (non-reflective) or slightly colored layer underneath a glassy surface. The surface is lustrous and transparent or tinted slightly green as seen in section, while the altered zone underneath is black with shiny metallic islands of remnant δ-phase. The very nature of the non-metallic surface layer seems to assure that the basic composition of the altered zone was present when the surface treatment was executed and the surface was "scaled" by applying the glassy surface layer. Warty corrosion, as seen at breaks and pits in the surface layer, lends credence to this statement. The amount of iron in the altered zone also suggests that the layer, when new, contained black or dark iron oxide.

A very interesting piece of evidence arose when we were examining mirrors by radiography for a projected catalogue on Chinese mirrors in the Freer Gallery of Art. The backs of at least three mirrors (F.G.A. nos. 09.275, 16.244, and 11.104) were seen to be black in some areas and silvery in others; these areas are related to the design. In Figure 10 we reproduce one of these mirrors (*a*) in normal light and (*b*) in diffuse reflected light ("tent" lighting). Most of the back of the mirror is black, but the decorative ring in the outer rim, the four bosses and four animals in the middle decor register, the ring around the central quatrefoil and the quatrefoil itself are silver in color. The front of the mirror has apparently been repolished. The selective coloration of the back must be intentional. While mirrors with adventitious black areas, possibly due to corrosion, are also known, it seems certain that the mirror in Figure 10 has been colored to enhance the design.

Subsequent to our discovery of the particolored nature of these mirrors, we noticed a photograph of a mirror from Ch'ang-sha, of the late Chou type, which has a design on the plain concave zone between the raised rim and the decorated back.[45]

The motif of double-pointed lozenges, so well known from early Han textiles, has been applied to the rim of this mirror in black and silver colors; at least, this is what the photograph seems to show. Controlled partial coloring, similar in intent to two-color gold and silver surface treatment, must have been within the technical competence of the Eastern Chou metalworker.

One further note on the material remains seems in order; we know of no reason for a

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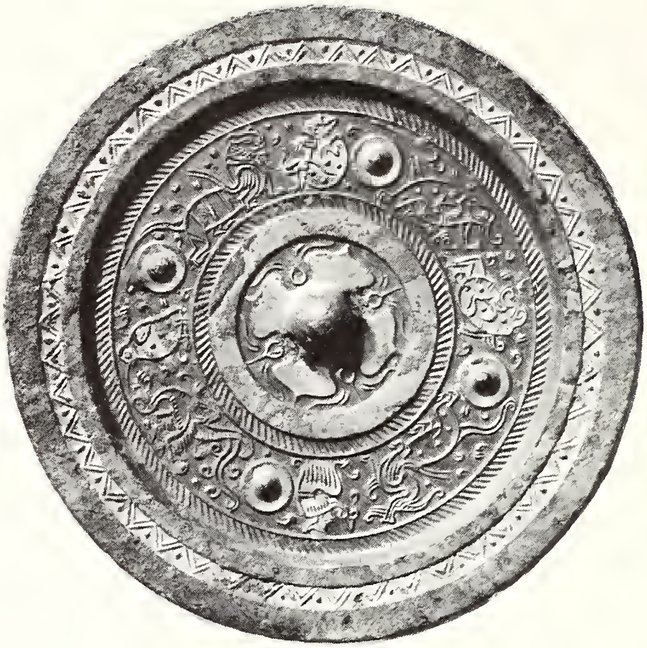
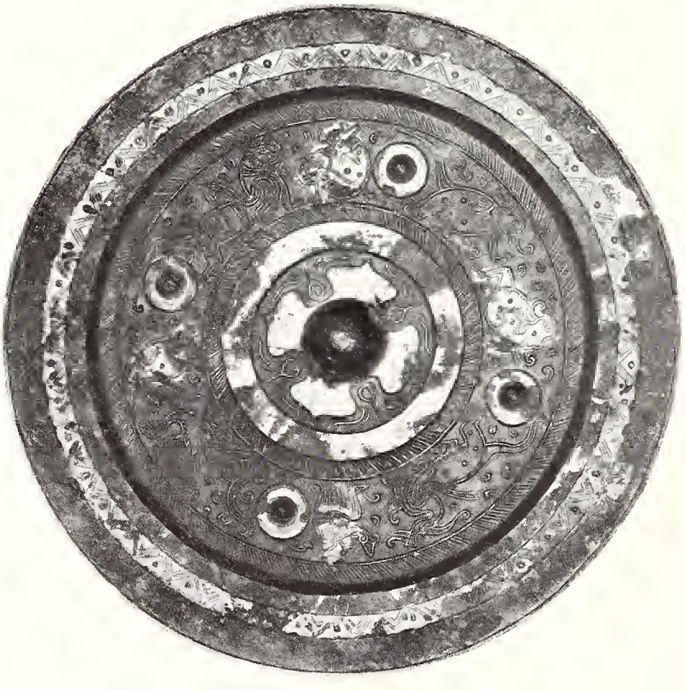
[45] Hunan Provincial Museum, *Ch'u-t'u T'ung-ching*, . . . no. 25.



a



b

FIG. 10.—Two views of a parti-colored mirror (Freer Gallery of Art 09.275, ×.6). *a.* shows the mirror in normal illumination for photography. *b.* shows the mirror in diffuse specular reflected light. The intentional nature of the silvery and black coloration is apparent.

mirror of the standard composition to corrode any differently from a bronze of slightly lower tin content, such as an ancient Chinese vessel. The range of colors and crusty, thick patinas seen on vessels is also seen on the non-black mirrors; when new, these mirrors would have been shiny silvery-white in appearance.

Documentary evidence. While there seem to be no literary sources giving information on the colors of weapons of the late Chou and Han periods, there are literary sources referring to mirrors. Many inscriptions occur on mirrors themselves; these often state that the mirror is bright (*ming*) or bright and shining (*ch'ing-ming*).[46]

In ancient literature, mirrors are often mentioned. Shen Pu-hai, the legalist philosopher of the fourth century B.C., is quoted as saying, "if a mirror has a flawless surface, then without any action, the beautiful and the ugly are revealed in it of themselves." In resembling a mirror, the mind was *ming* (brightly intelligent), or, presumably, *ch'ing ming* (totally clear and brightly intelligent).[47] In a poem by Hsü Kan (171–218 A.D.), the mirror occurs: "Since you went away/my shining mirror darkens with neglect"[48] or "Since you went away/my bright mirror lies dim, untended."[49]

Although the majority of literary sources talk of mirrors that are bright and shiny, some mention black mirrors. T'ang Shen-wei, a pharmaceutical naturalist writing in 1080 A.D., said that silver blackened by exposure to sulfur vapors for several days was used to make "dew-mirrors" for collecting dew at night.[50] The legendary personification of the sun is said to be looking for a bride, "black and shiny like a mirror."[51] It seems logical that black mirrors are mentioned in connection with the moon and night here.

One illustration of early mirrors may have some bearing on the question. It occurs in Ku K'ai-chih's painting, "Admonitions of the Imperial Instructress," in scene 6 shown in Figure 11.[52] On the left a lady, whose hair is being plaited by a servant girl, observes the process in a mirror. The mirror has a tasseled cord and is supported on a stand. It is, perhaps, a foot in diameter. The back, which we see in the painting, is dark or black and is plain with one relief line for decoration.

On the right, another lady adjusts her hair while looking in a mirror. We see her from the back. Her left hand holds the mirror, which shows a clear reflection of her face and upraised right hand. In painting this scene, the artist simply drew a thin black line to delineate the edge of the mirror and drew the face and hand of the lady within it. The painting communicates the bright, shiny,

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[46] W. Perceval Yetts, *The George Eumorfopoulos Collection Catalogue*, vol. 2, bronzes, bells, drums, mirrors, etc. (Ernest Benn, London, 1930) p. 30ff and p. 52; Watson, *Ancient Chinese Bronzes*, p. 96.

[47] Thomas A. Metzger, "Ultimate Wisdom, or Applied Psychology? A Review of Creel's Shen-Pu-hai," *Early China*, 2 (Fall 1976), pp. 20–21.

[48] Translated in Burton Watson, *Chinese Lyricism*, (Columbia University Press, New York, 1971) p. 45.

[49] Translated by Ronald C. Miao, ~~in~~ *Sunflower Splendor*, editors Wu-chi Liu and Irving Yuching Lo (Anchor Press, New York, 1975) p. 40.

[50] Joseph Needham, *Science and Civilization in China*, volume 5, part 3 (University Press: Cambridge, 1976), p. 31, Note a.

[51] Catherine Hoppe, "Deux miroirs d'epoque T'ang," *Cahiers de Mariemont*, no. 5 and 6 (1974–1975), pp. 21–30; Marcel Granet, *Dancses et légendes de la Chine ancienne*, (Librairie Félix Alcan, Paris, 1926). vol. 1, p. 507ff.

[52] The painting is now in the British Museum, London; see Osvald Sirén, *Chinese Painting*, (Lund Humphries, London, 1956) vol. 3, plate 13.

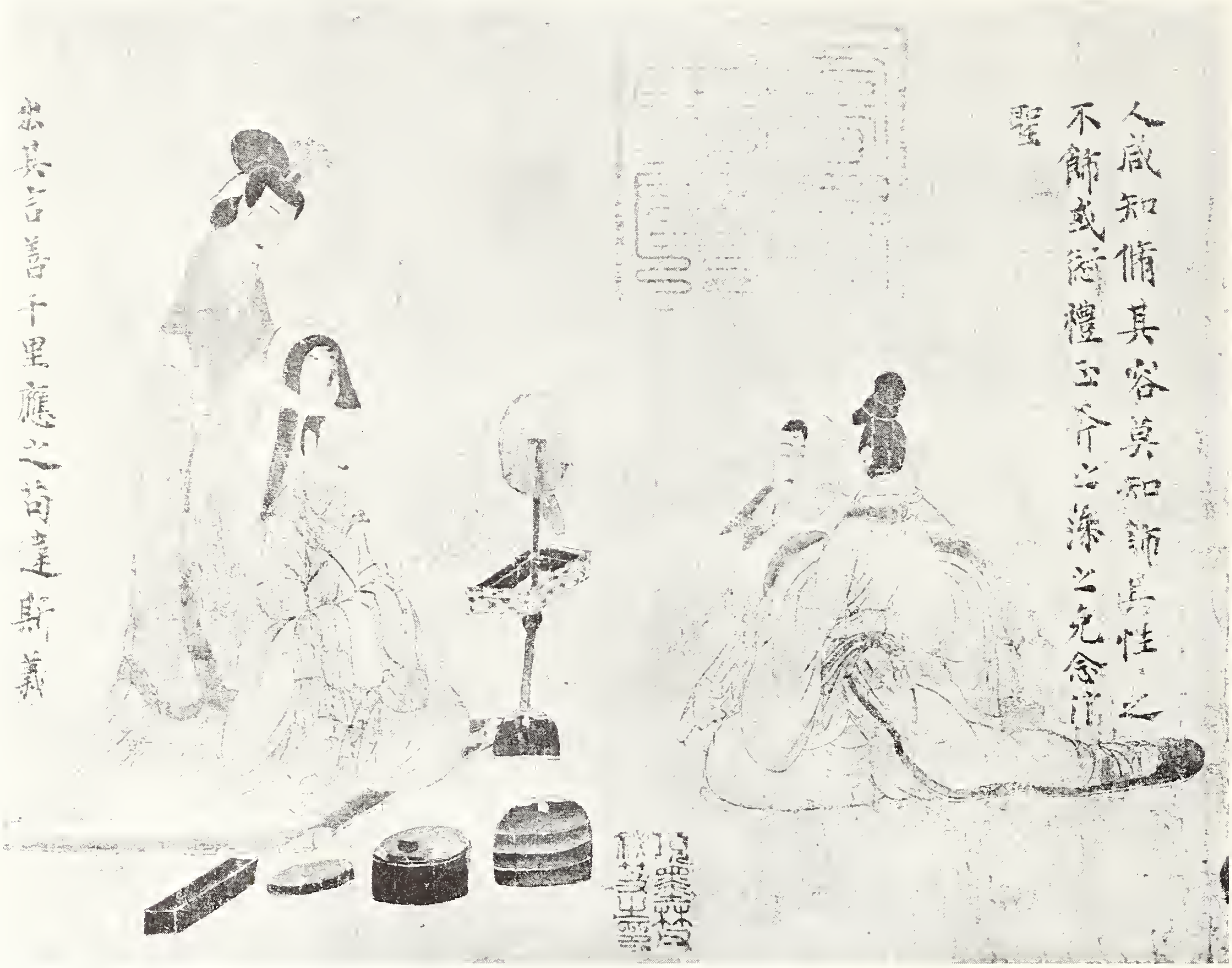
人咸知脩其容莫知飾其性之
不飾或愆禮正斧之藻之克念作
聖
出其言善千里應之苟違斯義

Fig. 11.—A detail of Ku Kai-chih's painting, "The Admonitions of the Imperial Instructress," showing two ladies at their mirrors (after Sirén); the original is in the British Museum.

clear reflection as we see it in polished speculum bronze, without any coloration at all.

Possible uses of black mirrors. Let us sum up the available evidence. Not all ancient Chinese mirrors have the mirror black surface. Mirrors with two-colored surfaces can be found. Mirrors with shiny white surfaces which have corroded can also be found; a shiny white mirror is represented in the Ku K'ai-chih painting.

What possible reasons would there be for mirrors to be black? As far as we can tell, mirrors were used in ancient China (late Chou and Han times) for the following purposes:

(1) Cosmetic uses—examining one's own reflection
(2) Collection of dew from the moon at night[53]

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[53] Joseph Needham, *Science and Civilization* . . . vol. 4, part 1 (Section 26), p. 87ff.

(3) Burial with the dead[54]
(4) Burning glasses[55]
(5) Optical experiments
(6) Magical purposes[56]

For cosmetic purposes, some mirrors were shiny and bright (not black) as we see from the Ku K'ai-chih painting and the quote from Hsü Kan's poem. Of course, the back could be black, but the face had to be shiny and reflective. Hsü Kan's poem also shows conclusively that some mirrors corroded in a relatively short time (months to years). These must not have had the corrosion-resistant black surface. The corrosion (and polishing) of cosmetic mirrors was, in fact, familiar enough that Hsü Kan could use it as a poetic metaphor.

Dew-collecting mirrors (or at least some of them) were black. While it is not clear when mirrors began to be interred with the dead as a symbol of light, the later uses, as de Groot outlines them, imply the use of bright mirrors.

Magical purposes do not, it seems to us, imply either black or silvery mirrors. It is not clear whether the surface-blackening and coating would disturb the light reflecting and focussing property of one of the so-called "magic" mirrors or not; our guess is that it would not.[57] Other magical powers are ascribed to mirrors by de Groot,[58] and it is unclear whether these uses would require light or dark mirrors.

It seems that, on the basis of the material evidence, the evidence from literary sources, and the pictorial evidence, mirrors must have been produced both in the silver-white color and the black color. The mirror of Figure 10, in fact, shows both colors on the back of one mirror.

PATTERN-ETCHED WEAPONS

Another group of bronzes with intentional surface coloration is formed by the pattern-etched weapons. We use the term "pattern-etched" to denote various sorts of surface treatment; some weapons have an all-over coloration, some are partly colored; some have patterns on the blade. Since there seems to be a connection with etching processes, we have decided to use the term "pattern-etched" to apply to the entire class. Watson[59] uses the term "variegated" to apply to these weapons, and says (referring to the Late Chou period):

> To the same enterprising time belong weapons—swords, *ko* and spearheads—decorated with mottling and figures such as the stars on the spearhead of Color Plate C. It is not known how the pattern was produced on the metal surface. Possibly the marks have been accentuated in the patina acquired by the bronze during burial. This *tour de force* of metalcraft may have been an achievement of the Ch'u foundries, for a large number of weapons decorated in this

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[54] J. J. M. DeGroot, *The Religious System of China* (E. J. Brill: Leyden, 1897) Vol. 2, p. 398; Vol. 1, pp. 45 and 93; Friedrich Hirth, *Chinese Metallic Mirrors, with Notes on Some Ancient Specimens in the Museé Guimet, Paris*, reprinted from the Boas Anniversary Volume, pp. 308–256 (G. E. Sechert and Company, New York, 1907).

[55] Joseph Needham, *Science and Civilization . . .*, Vol. 4, part 1 (Section 26), p. 90ff.

[56] De Groot, *The Religious System of China*, Vol. 5, pp. 1000–1005; also Needham, *loc. cit.*

[57] On "magic" mirrors, see Needham, *Science and Civilization* . . . Vol. 4, part 1 (Section 26), p. 90ff.

[58] De Groot, *The Religious System of China*, p. 1000.

[59] William Watson, *Ancient Chinese Bronzes* (Faber and Faber, London 1962), p. 66 and color plate C.

manner were recently excavated near Ch'ang-sha in Hunan.

While we have done much less work on pattern-etched weapons than on mirrors, it is worthwhile to compare the two for the light the comparison may throw on intentional surface patination. Some of the weapons are quite plain but, when made, were apparently finished in two different colors. The blade could be black and the handle green or the blade green and the handle black.[60]

While the patina may have changed in burial subsequent to use, the fact is that the two parts now have a different patina; this difference in patina is not related to changes in the metal composition nor anything else we can imagine with the exception of intentional surface treatment of part of the sword.

In Ch'ang-sha, swords of the above type have also been excavated, as have swords with a different-colored stripe running down the median ridge, *ko* with spots on the surface, *ko* with irregular curved patterns ("worm-tracks") on the surface, swords with lozenge-shaped surface decoration, etc.[61]

TECHNICAL STUDIES IN CHINA

The Ch'ang-sha excavation report also contains an analytical table of bronzes.[62] Two swords are listed as having 78% copper, 14% tin, and 1.5% lead, and 72% copper, 14% tin and 10% lead, respectively. A two-color striped sword was analyzed; the edge contained 74% copper, 18% tin and 1% lead, the inside ridge contained 78% copper, 10% tin and 10% lead. (Figures are rounded off from those in the excavation report[63]). A surface-decorated sword from Fu-ling, Szechuan province has also been analyzed. It contained 82% copper, 15% tin, and 1.3% lead.[64]

Another analytical study on weapons was jointly undertaken by the Shanghai Material Analysis Institute and the Technical Laboratory of the Shanghai Museum.[65] The study included three fragments of striped swords, which are of interest in comparison with those from Ch'ang-sha. The fragments showed clear lines of demarcation between the outer (tin-rich) metal forming the cutting edges and the inner (copper-rich) metal forming the spine. The lines run from one blade face to the other, parallel to the plane defined by the two median ridges on the blade faces. Lead in the metal of the spines varies from under 1% to over 10%. Lead is, however, kept low in the exterior cutting edges. The metals of the cutting edge and spine would be different in color, and would probably patinate differently. While we have no analyses of patina on striped swords, some of the high-tin edges appear to have the mirror-black patination. These swords show an excellent conscious control of metallurgy and properties of the finished object through composition. By casting a higher-tin outside onto a lower-tin spine,[66] the founder has put the metal with the desired composition and properties in the appropriate place. Knowledge and control of physical properties through composition (and the trade-offs involved) is clearly shown in literary sources from the Eastern Chou period.[67] It is also interesting how these swords presage in bronze the later development of iron swords in Japan, with their hardened cutting edges and toughened spines.

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[60] For black-bladed swords see the sword in the Hong Kong City Museum and Art Gallery (Reproduced in Chase, "What is the Smooth, Lustrous Black Surface . . ." p. 187 Figure Q-1-2), and sword #1943.52.6 in the Winthrop Collection, Fogg Art Museum, Harvard University; Winthrop Collection Sword Fragment #1943.52.7 has a fine, thick shiny black patina on the handle and guard.

[61] The Provincial Museum of Hunan, "The Ch'u Tombs of Ch'ang-sha," *Kaogu Xuebao* no. 23 (1959, #1), pp. 41–60 and plate IX, no. 1, 3, 4, etc.

[62] "The Ch'u Tombs of Ch'ang-sha", pp. 59–60.

[63] "The Ch'u Tombs of Ch'ang-sha", p. 48.

[64] The Szechwan Provincial Museum and the Chungking Museum (and Fu-ling Museum), "Excavation of the Warring States Open Shaft Tombs at Fu-ling, Szechwan Province", *Wen Wu*, no. 5 (1974), pp. 61–84.

[65] The results were seen by WTC on display in the Shanghai Museum in 1973 and subsequently confirmed by private communication (letter from Shanghai Museum, April 10, 1978).

The display cited in footnote 65 also included two pattern-etched weapons, one a spearpoint similar to that in the British Museum,[68] but with a diamond-shaped pattern, and the other a sword with plain hilt and no pommel, also with a diamond-shaped pattern.

> The X-ray analysis shows that the specimen from the surface of the sword contains, in addition to the normal chemical compounds of copper, tin and lead from the bronze, two parts of tin and one part of iron. The result demonstrates that the intaglio design is made of tin and iron. This method started late in the period of the Spring and Autumn Annals.[69]

This result shows the same effect as do our determinations on the mirrors; tin and iron are enriched in the surface layers.

PRESENT INVESTIGATIONS

The Brundage sword. This sword is Brundage Collection Number B60.B758 (fig. 12). One author (WTC) examined it closely at the Asian Art Museum of San Francisco on September 29 and 30, 1971. It is of a type very similar to an uninscribed sword from the excavations at Chiang-ling, shown in the Chinese Archaeological Exhibition which visited the United States.[70] The Brundage sword has a ringed hilt and attached disc pommel. The pommel and about 3 cm of attaching bronze were mortised and set onto a tenon running up from the hilt (this feature recurs on another sword from Chiang-ling).

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[66] It is not clear whether the outside or inside of these swords was cast first. The order above assumes casting of the higher-melting metal first. A striped and inlaid sword in the Freer Gallery (No. 29.19) shows radiographically that the inside was cast into the outside edges.

[67] In a book of ca. 240 B.C., the following passage occurs: "A swordsmith said, 'white metal [tin] makes a sword hard, yellow metal [copper] makes it elastic. When yellow and white are mixed together, the sword is both hard and elastic and these are the best ones.' But he argued with him, saying, 'the white is the reason why the sword is not elastic, the yellow is the reason why the sword is not hard. If you mix yellow and white together the sword cannot be both hard and elastic. Besides, if it were soft it would easily bend and if it were hard it would easily break. A sword which easily bends and breaks—how could it be called a sharp one?' Now a sword does not change its nature, yet some may call it good and some bad; that is only a matter of opinion." *Lü Shih Ch'un Ch'iu*, Chapter 150, Volume II, p. 158; Translated in Joseph Needham, *The Development of Iron and Steel Technology in China* (The Newcomen Society, 1964; Cambridge University Press, 1975) p. 1. The famous quote from the *K'ao Kung Ch'i* section of the *Chou Li* also shows knowledge of the properties of different copper-tin alloys; see Chase and Ziebold, "Ternary Representations . . ."

[68] See Watson, *Chinese Bronzes*, color plate C.

[69] Analytical result from exhibition label, translated by Celia Hsu, then Assistant Librarian of the Freer Gallery of Art, 1977; confirmed by private communication (see note 50).

[70] CPAM Hupeh Province, "Excavations at Chiang-ling Hsien, Hupeh", *Wen Wu*, no. 5, (1966), p. 36, Figure 13 and Plate 2: see also Anon., *Historical Relics Unearthed in New China* (Wen Wu Press, Peking 1972, late 69).

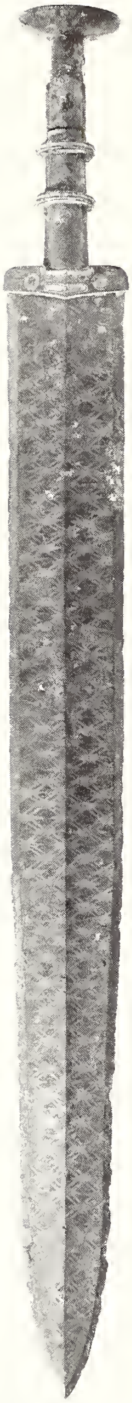


FIG. 12.—Pattern-etched sword in the Brundage Collection (#B60.B758). 55.1 cm long; grey-to-black with green patches and green handle (reproduced by the courtesy of the Asian Art Museum of San Francisco, The Avery Brundage Collection).

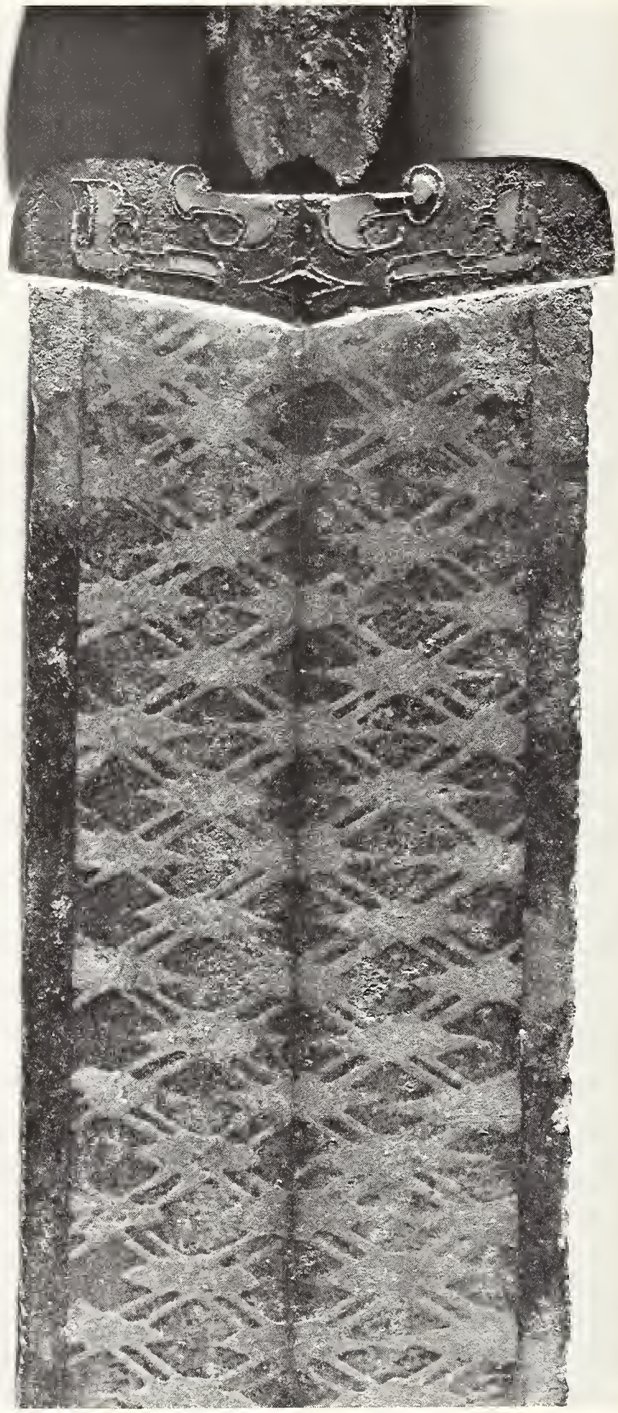


FIG. 13.—Detail of the blade of the Brundage sword, showing pattern-etching, possibly employing an etching resist. Ca. × 1.5 (reproduced by the courtesy of the Asian Art Museum of San Francisco, The Avery Brundage Collection).

The blade hilt and guard have corroded normally and now appear green; from the lower corner of the guard (where the surface drops down from the inlaid area of the guard to intersect the bronze blade), the surface is dark grey; this continues down onto the blade. Along the blade the surface is dark grey with occasional green corrosion products, as are the blade edges. The division between the green and grey areas is straight and sharp, and does not coincide with any change in the metal itself.

The design of the pattern is a double-line diaper with diamonds at intersections. The lines of the pattern are beautifully straight and regular (fig. 13); a straightedge can be laid along the lines. The diamonds, however, are not as regular; their edges are ragged where the lines intersect them. In this case, resist etching is a definite possibility. If one takes a fairly hard resist and attempts to scratch this sort of pattern into it (as we have done), the resist tends to break up along the directions of the lines as the diamonds are scratched in. From examination at higher magnifications, it is apparent that the lines and diamonds lie below the background. The pattern is matte black, and much less shiny than the background (fig. 14a). Where the pattern intersects the edge of the sword, small, dark, almost uncorroded areas can be seen (fig. 14b), which suggest that the sharpening of the beveled edges has cut through the structure of the pattern.

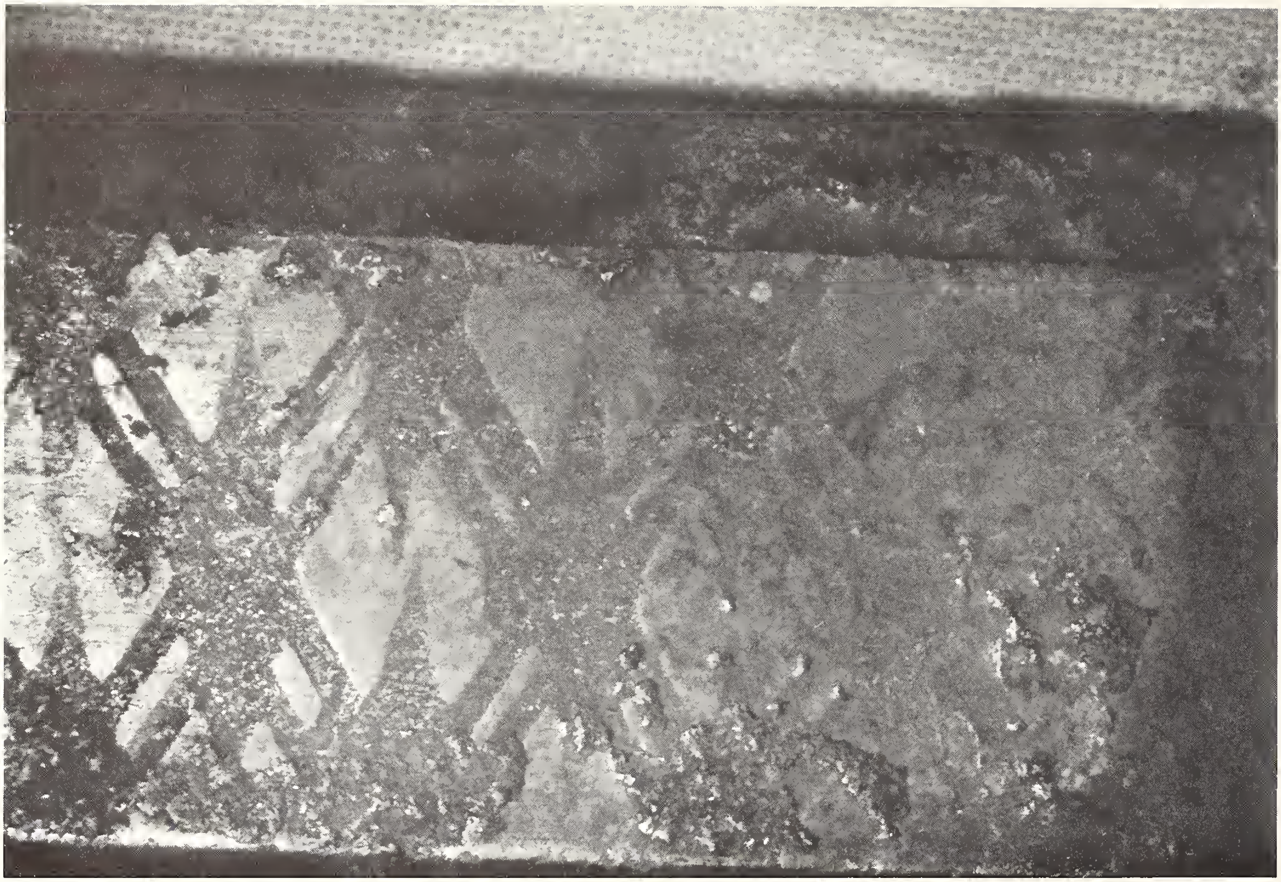
The normal cast dendritic structure of a Chinese bronze shows on this sword, and can be clearly seen under even moderate magnification. Dendrites run continuously through both etched and unetched areas, and through the dark spots on the beveled edges. In the pattern-etched areas, however, the α-phase of the dendrites stands above the δ-phase which has been removed (figs. 14c and 14d). This suggests an etch like a strong acid, which would remove the tin-rich δ-phase first.

While the above observations of the sword's surface have not been confirmed by sectioning for metallurgical analysis or by replication, they strongly suggest that etching was used to produce the pattern, followed by darkening the surface of the blade.

The Garner spearpoint. The pattern-etched object we have examined most extensively is the Garner spearpoint, Freer Gallery of Art number SC-B-88, (fig. 15). The spearpoint is predominantly green, with a brown pattern of five-pointed stars on the blade. It is 24.4 cm long and 3.7 cm wide and weighs 174.4 grams. A prominent median ridge is present, along with animal masks on the sides of the socket and four double-spiral figures in intaglio on the lower sides of the socket. The beveled edges are free of patterning.

Figure 16 shows a reproduction of an X-radiograph of the spearpoint. The original radiograph was reproduced by contact printing; thus, the light and dark values are reversed. Three major breaks were revealed; the break near the socket has been repaired with lead solder. No repair material was apparent in the upper two breaks, and we found that a wooden reinforcement had been put inside the interior cavity with plaster; neither material shows on the X-radiograph. The pattern-etched design is just visible in the central area; porosity can be seen throughout the blade, and the regular shape of the interior cavity is nicely visible.

After radiography, the object was disassembled along the old breaks and, after photography of the surface, a section was taken slightly over halfway through the blade.



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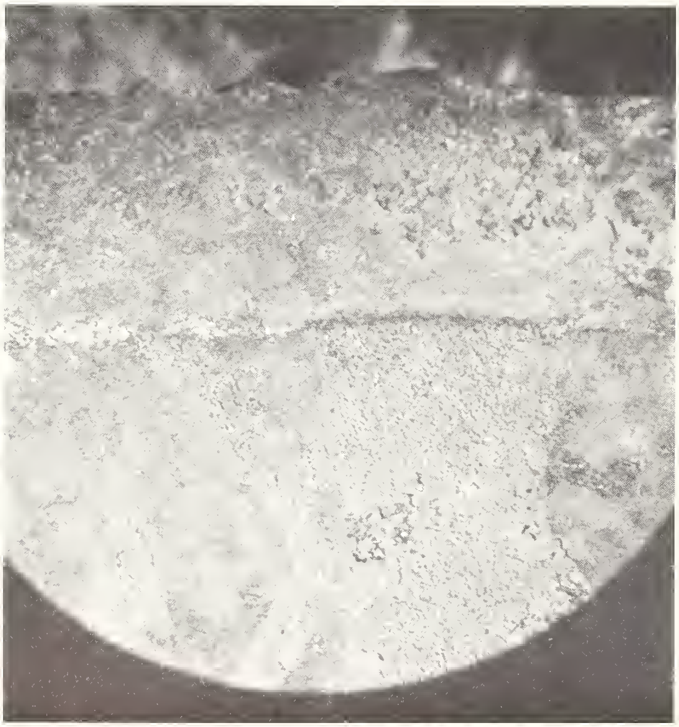

b

Fig. 14*a–d*.—Four magnified details of the Brundage sword *a*. Blade and edge of sword, showing sunken nature of lines, ×6.75. *b*. Edge of sword, showing corrosion-resistant area, ×18. *c*. Edge of sword, showing dendrites in pattern-etched area; the α-phase remains, ×39. *d*. Another area similar to 12*c*, showing the continuity of the dendritic structure from the sharpened area throughout the corrosion-resistant area into the etched area; ×39.

c

d

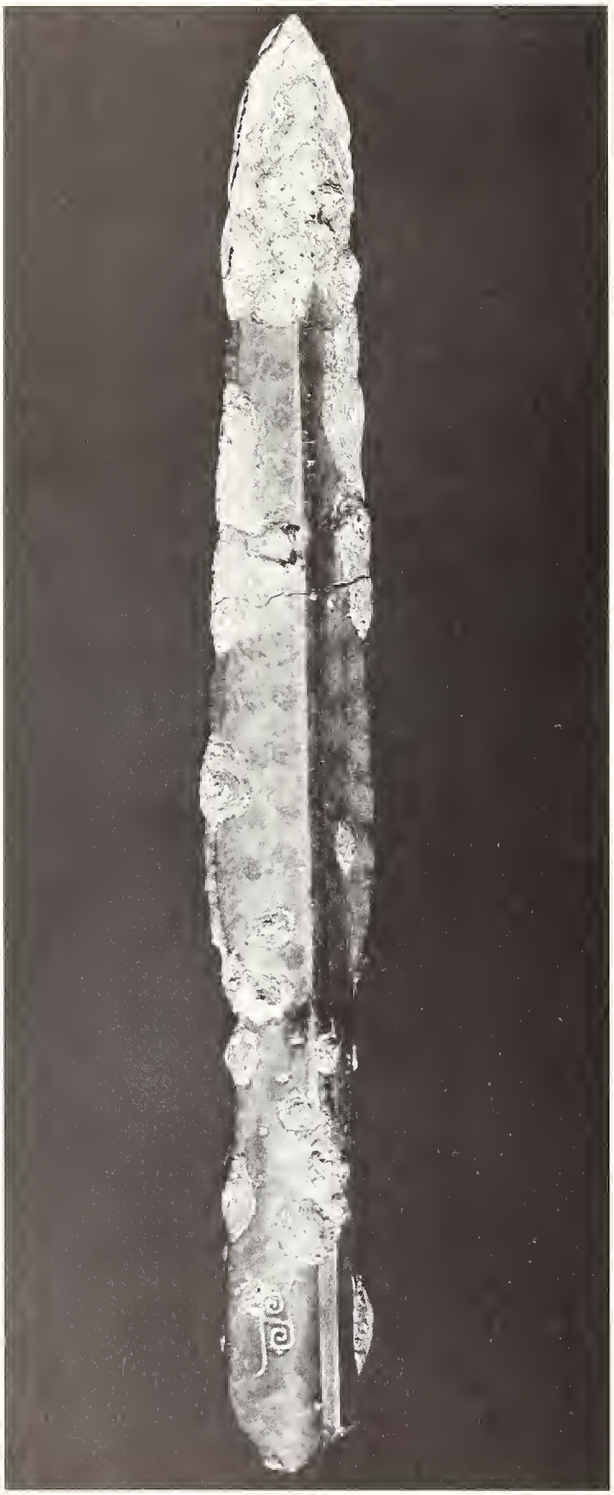

Fig. 15.—The Garner spearpoint (FGA SC-B-88), showing corrosion and surface decoration; slightly reduced.

The upward pointing arrow in Figure 17 shows the area sampled.

A polished metallographic section was made of the sample, and an all-over view is shown in Figure 18, in bright-field, unetched, taken from a photomosaic made at ×20 magnification. The section shows the blade edge on the left and the median ridge at the top. Much cracking and intergranular corrosion can be seen. The most corrosion has occurred at the blade edge. Corrosion can also be seen to be penetrating along cracks in the metal. The dendritic cast structure is clearly revealed by natural corrosion etching.

In a closer view of the sharpened blade edge, Figure 19a, bright field, unetched, we can see that the corrosion along cracks at the blade edge is proceeding with the δ-phase first and the α-phase second, i.e., the tin-rich phase is corroding first, leaving the copper-rich phase in place. Areas of redeposited copper, especially in holes (due to casting porosity or lead removed by corrosion) can also be seen.

When we move to an intact area of the blade, however, we can see that the corrosion or surface treatment on the outer faces of the object has proceeded by the inverse corrosion process. Figure 19b shows an area contiguous to that shown in Figure 19a. The tin-rich δ-phase remains just under the outer (lower) surface.[71] The same corrosion phenomena are seen in the black mirrors.

A polished thin section was then made from the sample shown above, so that the corrosion phases could be studied in transmitted light. A sample from the crack shown in Figure 19b at the lower right shows clearly the difference in the two types of corrosion (fig. 20). Figure 21 shows a similar area at a

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[71] Chase, "What is the smooth lustrous surface . . ." Figures Q-1-13 to Q-1-17.

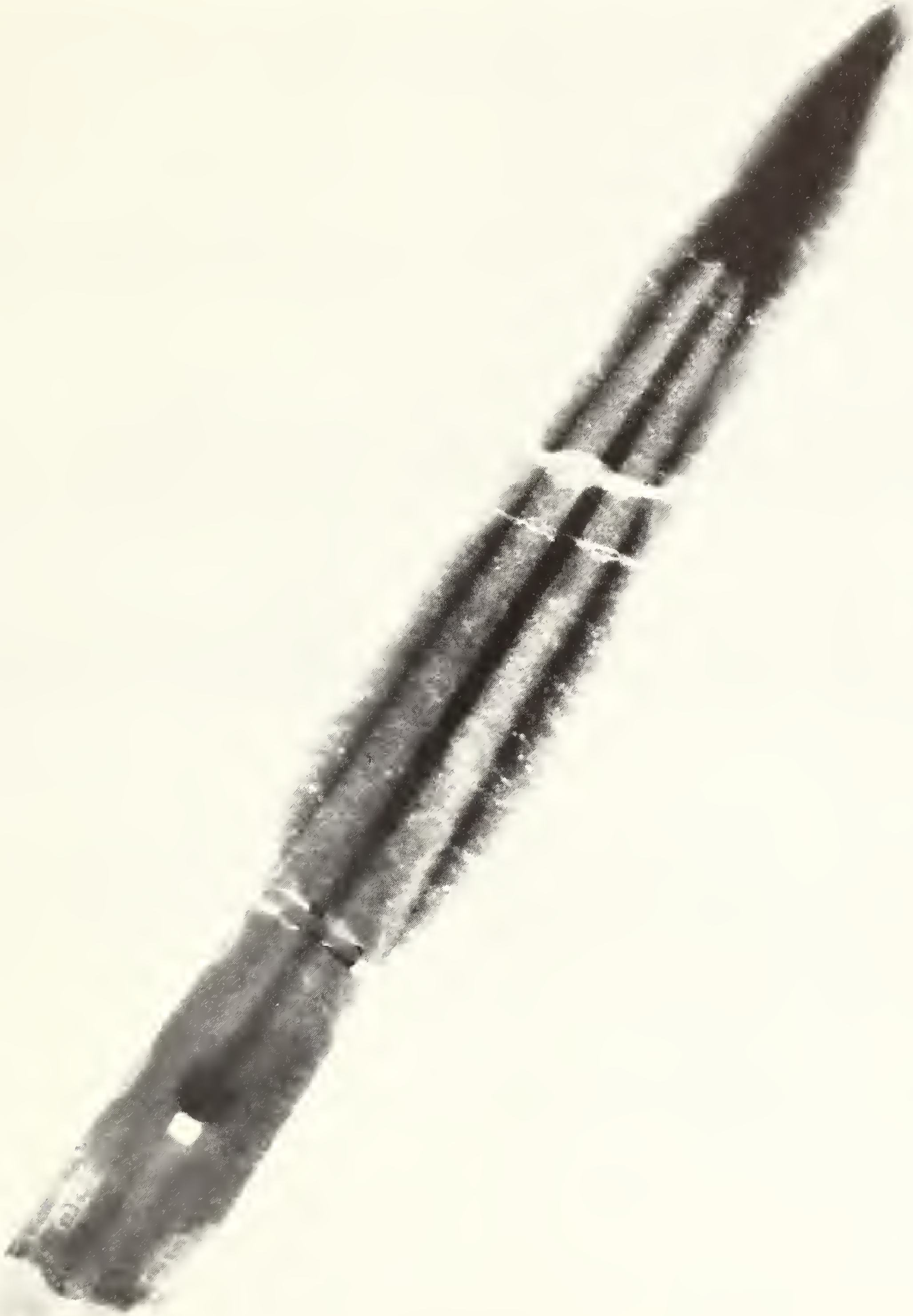


Fig. 16.—Negative reproduction of a radiograph of the Garner spearpoint, showing the interior cavity, breaks and repairs, etc. Radiographic conditions: FGA Radiograph #151, done at Naval Ordnance Laboratory, 8/2/71. 200 kVP (self-rectified unit), 10 mA. Exposure time: 1 minute. Tube—film distance, 6 ft. Type M film, X-omat development. Lead screens used. Actual size.

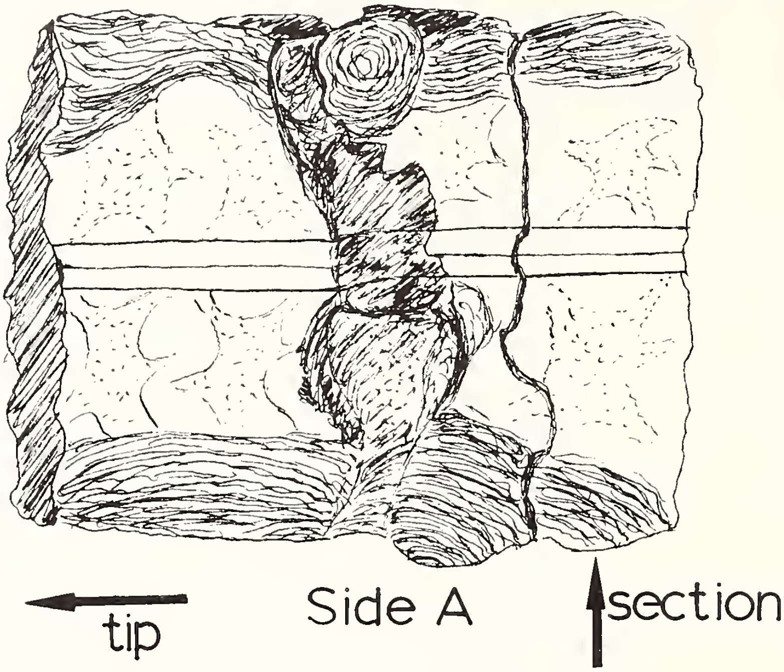


Fig. 17.—Drawing showing area sectioned on Garner spearpoint. The upward-pointing arrow shows area sectioned.

lower magnification, in a combination of bright-field reflected and bright-field transmitted illumination. The clear, greenish surface layer exhibits no birefringence in crossed polars, and appears to be isotropic. The glassy phase seen on the outer surface of this weapon also appears on polished thin sections of mirrors. Underneath the glassy phase, and interpenetrating with it, is the altered zone produced by the α-removal type of corrosion. Areas under the brown five-pointed star design on the surface can be seen in cross section to be more deeply corroded. This is the only visible difference between design and plain areas on the surface; it corresponds to the X-radiographic appearance of the design as barely visible radiotransparent areas on the film. Less metal is present under the design, but the entire weapon has a glassy, isotropic surface.

The thick corrosion crust visible on the surface of the object (fig. 15) tends to bear out the idea of an intentional surface coating applied after etching. The corrosion is warty, as on the mirrors. It occurs in areas where the surface contour turns sharply, as on the spine, or where any surface film would tend to be damaged mechanically, as at the tip and sharp edges of the weapon. These cracks and breaks would allow the corroding medium freer access at these points, and promote corrosion: cold-working, an alternate reason for greater corrosion, is not present (fig. 19a).

In this case, we can accept the idea of a pattern-etching followed by sharpening and then all-over surface treatment applied to the entire outside of the weapon. The interior shaft hole shows no signs of surface treatment.

A spearpoint from the Bishop Collection of the Freer Gallery (X18) was sectioned and examined with the electron microprobe; while the examination of this object is not yet complete, the initial conclusions agree. The black and green shiny surface is depleted in Cu and enriched in Sn, Fe and Si. The pattern-etched weapons, while more varied

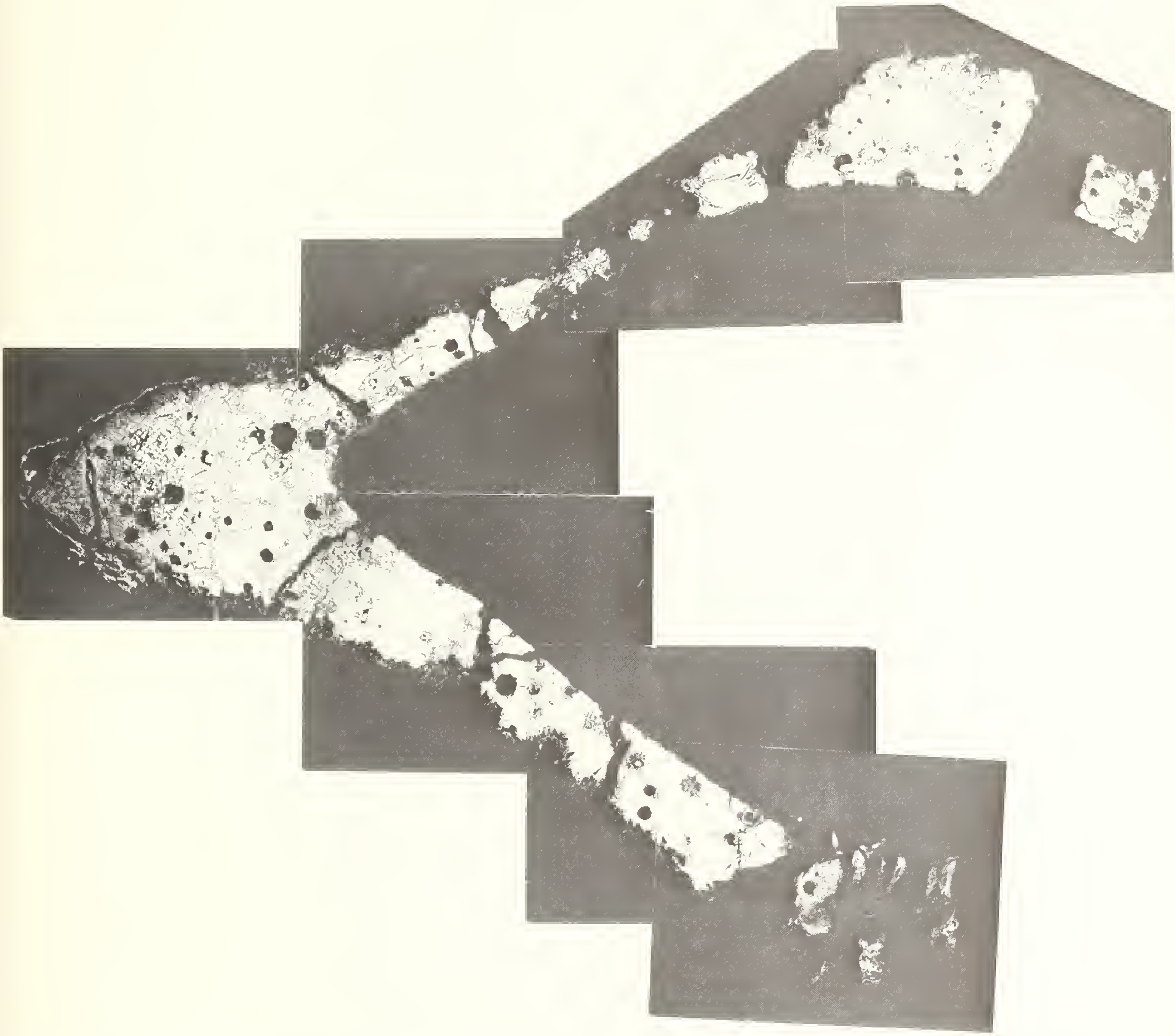
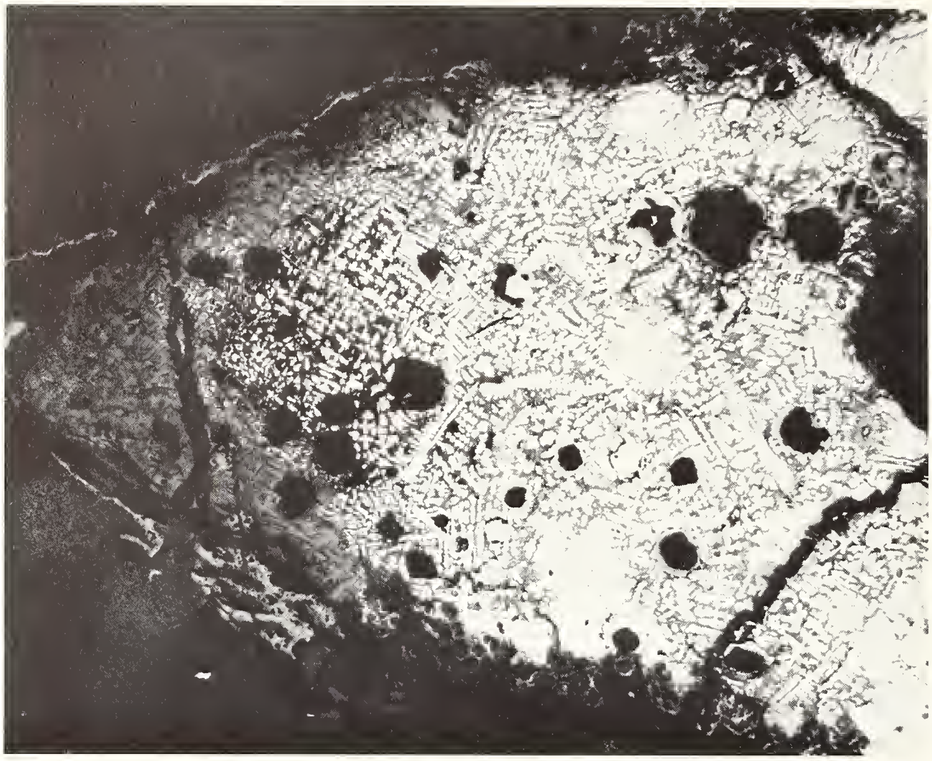
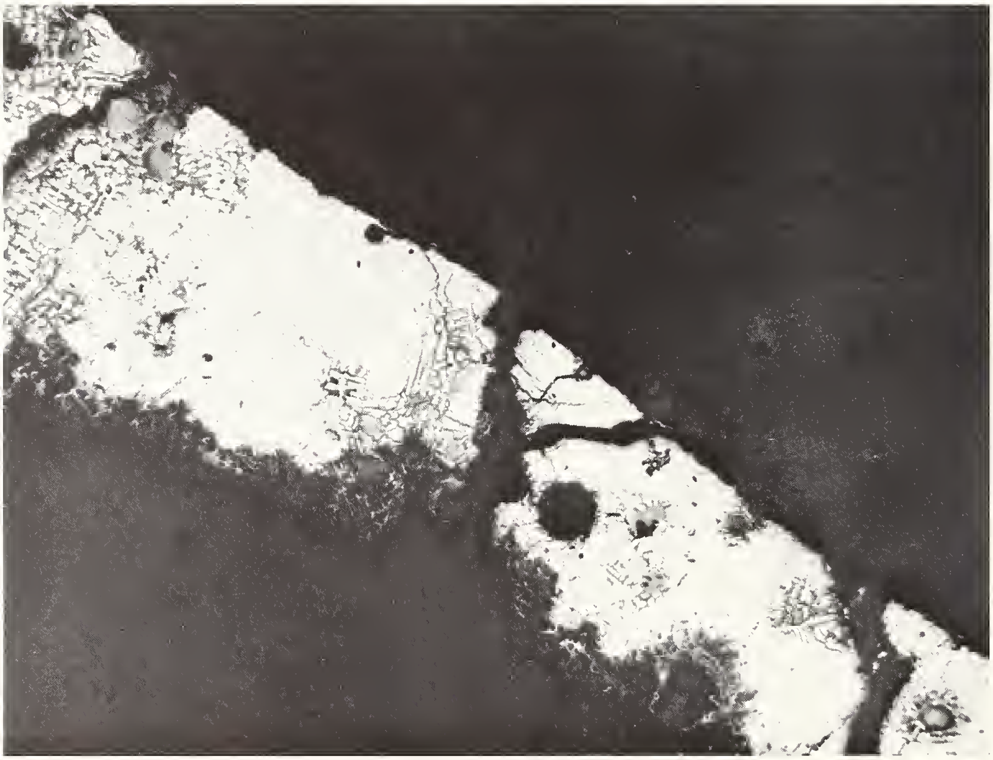


Fig. 18.—Composite metallograph of the Garner spearpoint, ca. ×4, bright field, unetched; the sharpened edge is at left.



a



b

FIG. 19.—Two metallographs of the Garner spearpoint, ×17, bright field, unetched. *a*. Shows the sharpened edge with interior corrosion of the δ-removal type, redeposited copper, cracks, etc. The interior cavity is to the right. *b*. Shows the wall on the blade side of the weapon, the interior cavity is towards the top; note the absence of δ-removal corrosion except at cracks and breaks. The altered surface is towards the bottom of the photograph.

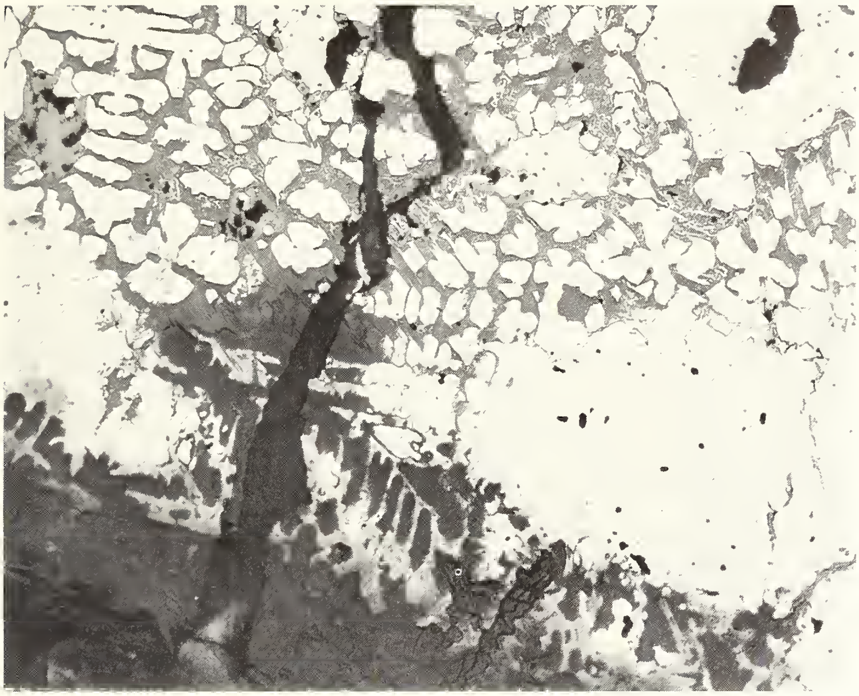


Fig. 20.—A magnified view near the area shown in Figure 19. Note δ-removal corrosion near the crack; the outer surface is shown at the bottom. Remnant δ-phase can be seen under the glassy surface. × 100, bright field, unetched.

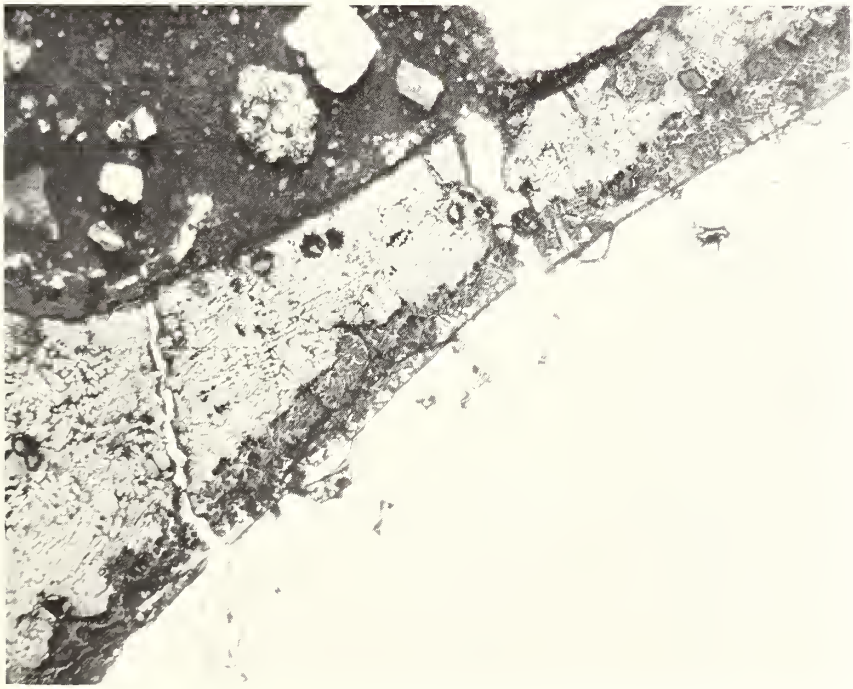


Fig. 21.—A less magnified view in a combination of bright field polarized reflected light and transmitted light (×22, unetched). The glassy layer can be seen on the lower portions of the specimen.

than the mirrors, certainly point to carefully-controlled surface treatment.

POSSIBLE TECHNIQUES OF SURFACE TREATMENT

THE RANGE OF CHEMICAL SURFACE TREATMENTS

We have shown above that, in the late Chou and Han periods in the Ch'u culture area, mirrors were produced with black surfaces, silvery metallic surfaces, and combinations of these two treatments. Weapons were made with etched decorations, partly metallicized surfaces, and also blackened. From the evidence above, we hypothesize that at least four separate processes of chemical surface treatment were in use:

(1) General surface blackening
(2) Pattern-etching
(3) Spot coloration
(4) Application of a thin, glassy surface layer.

These processes could be applied singly or in combination. Other means of surface coloration were known in ancient China; mirrors occur with gilded, inlaid, and painted surfaces. Indeed, paint resembles the "mirror black patina" in being an applied nonmetallic surface. Belt-hooks with gold and silver inlay, gilding in two colors, and stone and glass inlay can be seen in many collections. It is evident that interest in surface coloration and decoration of bronzes was widespread.

This interest in sumptuary encrustation of metals can be clearly seen in objects from the Man-ch'eng tombs.[72] In addition to many gilded and inlaid bronzes, a number of color and surface variations of the bronze metal itself have been found here. Since the tombs were apparently quite dry and well-sealed, and since they were located in a northern area where corrosion is less active than in South China, it seems that the only way to explain the extensive variation in the bronze surfaces lies in the hypothesis of surface treatments of the kinds we suggest.

For example, of three mirrors found at Man-ch'eng, two were shiny black and one a a corroded green. The shiny black ones could have had an application of the surface blackening technique (1) followed by surface glazing (4). The corroded mirror may well have been only silvery when new. The large gold-inlaid *Po-shan-lu* censer has a velvety matte black surface which contrasts with the shiny gold. This could be an example of surface blackening, without the glassy coating. A bronze sword with glassy appearance could show application of the glassy coating on polished metal; some of the other swords have what appear to be glazed edges. We have seen no examples of etched decoration from Man-ch'eng although the manufacture of the dotted *ko* could have involved etching or selective blackening: having no technical evidence to cite, we cannot be sure. A wide variety of very sophisticated metal coloring and finishing processes were employed in these examples of former Han metalwork.

POSSIBLE METHODS USED

While the presence of gilding and inlay is easily recognized after even 2000 years of corrosion, the chemical surface treatments hypothesized above share aspects of natural corrosion processes. The remains of these treatments are easy to confuse with the results of long-term corrosion; corrosion has also made the task of reconstruction of the intentional processes far more difficult.

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[72] See note 42.

All of the chemical processes seem to have been employed for surface decoration after fabrication, or in the last steps of the fabrication process. Mirrors show polishing scratches under the glassy surface layer; the weapons seem to have been etched or surface-decorated, sharpened, and then given their protective surface coat.

The surface blackening and production of the "altered zone" must produce iron enrichment in the altered layer and must remove the copper-rich α-phase, leaving the δ-phase uncorroded. From the penetration of the "altered zone" into surface cracks and from its evenness, it seems that some sort of leaching or cementation process may well have been the technique employed. Since the α-phase at the surface is completely removed, however, and since the metal has not been appreciably heated to an elevated temperature, the process could have taken place in a solution at a relatively low temperature. Ferric chloride (which could be prepared from rust with wine vinegar and salt) will attack the α-phase and turn it brown. Perhaps a prolonged 'etch' would produce the effect of the altered zone.

For etching of the weapons, natural plant acids or an acidic natural salt solution from something like ferrous sulfate may have been employed. Acidic extracts prepared from dried plums were long employed for cleaning ancient bronzes in China.

The spot-coloration techniques appear to be the results of selective tinning; although the experimental evidence for selective tinning is skimpy at the moment, the spots on the Bishop spearpoint look metallic in section; the *ko* from Ch'ang-sha mentioned above have had spots or drops applied; these could have been metallic tin. More proof is necessary on this point.

The production of the glassy surface layer is most difficult to explain. Possible candidates for the "glazing and sealing" process might be a dip in a hot melt of glazing material, rapid heat fusion of a ground frit on the mirror surface, pickling of the surface (producing the "altered zone"), followed by a fusion of the pickled material on the surface (possibly with a flux addition) or a cementation process. Sulfide blackening is ruled out by the appearance of our sulfur prints (above), and by the microprobe analysis. The sulfur distributions in the mirrors occur as sulfide inclusions, remnants from the original ores, and are unrelated to surface treatment. Because of the sharp line of demarcation of the dark material on such weapons as the Brundage sword, and because of the all-over evenness of the coloration, cementation seems the most likely process. Cementation is still being used to produce glassy surfaces on Iranian faience beads.[73] One limit on the glazing and sealing process is that it must have been performed at low temperature; the microstructure of the bronze looks normally solidified, with no evidence of later heat treatment.

None of these processes sounds particularly convincing at the moment; all need to be experimentally studied. We are, inevitably, confused by the effects of time on these objects. Significant alteration takes place during burial as well as in the fabrication process. In fact, we may be defining our sphere of interest too narrowly. Perhaps we should look more closely at all surface-decoration processes employed in this period (painting, gilding, gilding in two colors, etc.) to see if we can find any clues in information on related crafts.

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[73] Hans E. Wulff, Hildegard S. Wulff, and Leo Koch, "Egyptian Faience—A Possible Survival in Iran," *Archaeology*, vol. 21, no. 2 (April, 1968), pp. 98–107.

THE HISTORICAL CONTEXT

While we cannot yet reconstruct, to our satisfaction, the technique involved in chemical surface treatment of bronzes, we can state beyond any reasonable doubt that such intentional surface treatments were practiced in late Chou and Han times. The bronze-maker's art in China undergoes a change from the late Shang and Early Chou. The early emphasis on size, forms which arise naturally from piece-mold casting, and surface decoration which emphasizes the mass and cast shapes of the vessel is replaced by an aesthetic of surface treatment and richness. The number of finishing techniques for metal increases greatly in scope and sophistication.

If we look at other facets of late Chou culture, the same increase in elaboration and sophistication can be seen. Mercury was distilled for the first time.[74] Although the possibility exists that metallic mercury was known earlier in the Near East, its use for fire gilding seems to appear first in China and then to travel through Persia to Egypt and the Roman world.[75] Lost-wax casting seems to begin in China during this period.[76] Glass production starts also.[77] Many of the classic Chinese scientific and alchemical texts date to the Late Chou,[78] as do well-known developments in philosophy, religion, music, war, poetry, representational art, sculpture, and so forth. Probably the most important development was the establishment of the Chinese bureaucratic system of government, which determined the later course of China and her science and technology.[79]

It is difficult to determine the causes of these innovations, or even (at this remove) to say which are causes and which are effects. Since, during the late Chou period, China was broken up into a number of separate kingdoms (the "Warring States"), commerce between them was handled by a rising and upwardly mobile merchant class.[80] Demand from this class influenced the production of sumptuary arts, and must have increased pressure for innovation in metalworking.

Another technical innovation with far-reaching consequences was the development of iron and steel. Iron production begins in China around 600 B.C. and rapidly burgeons into a major industry.[81] The increasing employment of iron must have changed the role of bronze more to that of a metal primarily for ornamentation and display, and thus must have given impetus to improved methods of surface finishing.[82] The higher temperatures required for casting iron and the waste materials made available by the iron industry may also have contributed to the possibilities for metal treatment.[83] We should not forget, either, that the "altered zone" and surface on the black mirrors is enriched in iron.

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[74] Joseph Needham, *Science and Civilization in China*, Vol. 5, Part 3, Section 33, p. 4.

[75] P. R. S. Moorey, "Some Ancient Metal Belts: Their Antecedents and Relatives," *Iran*, Vol. 5 (1967), p. 96; P. A. Lins and W. A. Oddy, "The Origins of Mercury Gilding," *Journal of Archaeological Science*, vol. 2 (1975), pp. 365–373.

[76] W. Watson, *The Genius of China*, p. 78.

[77] C. G. Seligman and H. C. Beck, "Far Eastern Glass: Some Western Origins," *Bulletin of the Museum of Far Eastern Antiquities, Stockholm*, no. 10 (1938).

[78] See note 74, above.

[79] Joseph Needham, *Science and Civilization in China*, Vol. 1, p. 94ff and p. 100.

[80] Hsü Cho-yun, *Ancient China in Transition* (Stanford University Press, Stanford, California 1965) p. 127ff.

[81] Needham, *The Development of Iron and Steel Technology in China*, passim; K. S. Chang, *The Archaeology of Ancient China* (Yale: New Haven, 1968), pp. 313–316 and 391; Cheng Te-k'un, *Archaeology in China Vol. 3, Chou China* (W. Heffer & Sons, Cambridge, 1963), pp. 247–249; recent bibliography collected in Li Chung's article elsewhere in this volume.

The technology of metalworking and metal production (the large-scale manufacture of metal objects and implements) made great strides forward in late Chou times. Metal production is, of course, directly related to ore sources and the metals trade. This may supply us with one reason why the mirrors, with their high-tin alloy, and the high-tin swords, are connected with the State of Ch'u. Many mirrors state, in their inscriptions, that they are made of "metal from Tan-yang."[84] Tan-yang was the first capital of Ch'u, and even in the early first century B.C. was still mentioned as being in the Ch'u region.[85] Modern tin mines are located in South China, in Fukien, Yünnan and Kweichow provinces, with other mines such as the Shui-kou-shan lead and zinc mine located in Hunan, more directly in the Ch'u culture area.[86] In fact, the city of Kuei-hsien, Yünnan, where over 100 mirrors were found, still has an active lead or tin mine.[87] Ch'u was also on the way to the rich tin fields of Malaysia. Tin (as an alloy constituent and as a surface coating) was, probably, more easily available in Ch'u than in the North.

Much more research must be devoted to present and past ore sources in China and their influence on metal production.

The history of Chinese metal technology remains to be written. We are only beginning to gain some insight into the processes and sophistication in use of materials available during the late Chou and Han periods.

The period of the 'hundred schools' of philosophers seems to be the equivalent of the European Renaissance, although the birth here springs, rapid and full-blown, from the Warring States and their background of political turmoil. Experimentation in thought, in the arts, and in technology was widespread. What were the reasons? Was it the free commerce between the various states with their fluid and changing borders? Was it the growing merchant class, socially climbing and interested in the sumptuous arts? Was it the leavening influence of barbarian and nomadic invasions and customs? Whatever the forces driving late Chou and Han art may have been, the material remains speak to us of lost skills and processes. One can but marvel at the craftsmanship and inventiveness of the ancient Chinese.

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[82] The transition of bronze weaponry from practical to ornamental use can be seen in the decrease in tensile strength of the alloys used in its manufacture. See Chase and Ziebold, "Ternary Representations . . ."

[83] It is interesting in this connection that a list of materials for making mirrors for presentation to the Great Buddha of Tōdaiji, now preserved as a handscroll in the Shōsōin, mentions the use of the powder given off when iron is forged on an anvil for polishing mirrors. The iron oxide derived from forging, after particle sizes had been controlled by levigation, might not be unlike modern rouge. Masaki Nakano, "Bronze Mirrors of the Nara Period: The Tōdai-ji Chūyō Yōdo Bun'an (Drafts for documents concerning mirrors for the Tōdai-ji Temple) among the archives of the Shōsōin," *Museum* (Tokyo) no. 190 (January, 1967), pp. 2–14, no. 192 (March 1967) pp. 2–13.

[84] A. Bulling, *The Decoration of Mirrors of the Han Period: A Chronology*; Artibus Asiae Supplementum XX (Artibus Asiae, Ascona, Switzerland 1960) p. 46.

[85] Chang, *Archaeology* . . . , p. 395; Burton Watson, *The Grand Historian*, p. 153.

[86] Chiao-min Hsien, *Atlas of China*, ed. Christopher L. Salter (McGraw-Hill: New York 1973), p. 99.

[87] See the quote from Barnard in note 34 above, also.

ACKNOWLEDGMENTS

Since our fascination with the black mirror problem has lasted more than a decade, there are many who have stimulated and supported us. Special thanks go to Cyril S. Smith, Emeritus Professor of the Massachusetts Institute of Technology, for his longstanding interest in our research and for reading the manuscript prior to publication. We are indebted to the curators and staff of the Far Eastern Department, Royal Ontario Museum, for their help in our study and for permission to use photographs of objects in the museum.

WTC would particularly like to thank the staff of the Freer Gallery of Art. The Technical Laboratory staff has been very helpful; Lynda Zycherman, in addition to discovering the bi-colored mirrors, has assisted in reviewing old notes and extensive files on the mirror problems collected by Gettens; and Elisabeth FitzHugh took some of the photomicrographs reproduced here. Jim Horns, formerly a summer intern in the laboratory, made the fine drawing of the Garner spearpoint. Raymond Schwartz and his assistants in the photographic laboratory were indispensable, and Celia Hsu and Ann Yonemura helped with translations. Grover Moreland of the Mineralogy Division of the Smithsonian made the polished thin section of the Garner spearpoint. The great generosity and scientific curiosity with which Sir Harry Garner presented the spearpoint to us are gratefully acknowledged.

WTC would like to thank the staff of the Asian Art Museum of San Francisco, especially Yvon d'Argencé, Director, Roger Broussal, Conservator, and Alexis Pancovic, Assistant Conservator, for their great assistance to him while he was in San Francisco in 1971, for allowing him to use their laboratory facilities, for making the photographs for Figures 10 and 12 available, and for allowing him to publish this account of their sword. Kazuo Yamasaki of Nagoya University graciously supplied a photographic copy of one of the Shōsōin documents.

UMF wishes specially to acknowledge the help of Mrs. E. Mutterer for her work in metallography and photography and the continuing support of the Chairman of the Department of Metallurgy and Materials Science, University of Toronto. Part of the work was supported by a grant from the National Research Council of Canada.

STUDIES ON THE IRON BLADE OF A SHANG DYNASTY BRONZE *YÜEH*-AXE UNEARTHED AT KAO-CH'ENG, HOPEI, CHINA*

By LI CHUNG**

In October 1972, the archaeologists of the Hopei Provincial Museum and the Hopei Commission for the Preservation of Ancient Monuments discovered, with the help of local peasants, a Shang Dynasty bronze *yüeh*-axe with an iron blade,[1] at Tai-hsi village in Kao-ch'eng County, Hopei Province. Most of the blade has already broken off and disappeared; the remaining tang, about 10 mm was embedded in the bronze slot. The overall dimension of the remaining *yüeh*-axe was 111 mm long and 85 mm wide (fig. 1). The axe dates back to the early stage of the Shang Dynasty remains at Hsiao-t'un in Anyang, which corresponds to about the fourteenth century B.C.

The discovery of this bronze axe with an iron blade is of great significance. It shows that as far back as three thousand three hundred years ago, the Chinese working people of the Shang Dynasty had already mastered the mechanical working of iron. An identification of the raw material of the iron blade would throw much new light on the origin and subsequent development of iron smelting in ancient China. But the task was complicated as the iron blade had completely oxidized without leaving any metallic iron. Judging by a sample taken near the surface of the remaining blade, the iron oxide seems to have a layered structure, and contains silicon-bearing and calcium-bearing particles. The fact that some of these particles appear to have a lamellar structure led to the archaeologists' suggestion in the original report that the iron blade might have been made of man-made iron.[2] On the other hand, chemical analysis of the iron rust on the surface layer shows that it contains 1.76% of nickel, which is equivalent to a minimum of 2.5% nickel in the metal matrix. The nickel content in the original metal should be even higher considering the losses during weathering. Although its high nickel content could have been the result of an accidental introduction of some nickel-rich mineral during smelting, all the ancient man-made iron

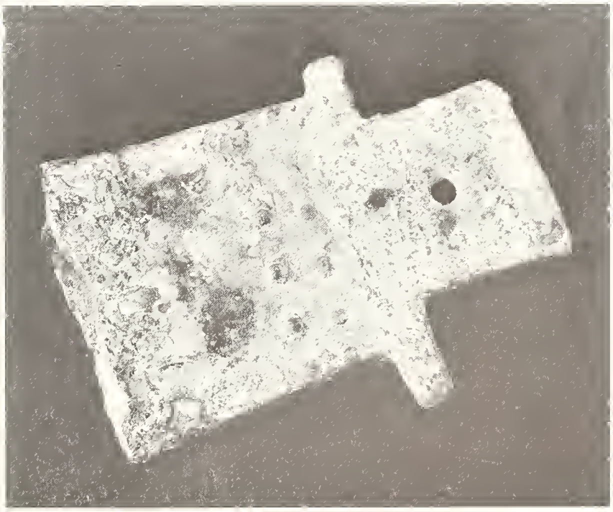

FIG. 1.—The Shang Dynasty bronze *yüeh*-axe unearthed at Kao-ch'eng, Hopei.

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* Translation of an article originally published in *Kaogu Xuebao*, 1976, No. 2 (No. 45 in overall sequence), pp. 17–34.

** Peking Institute of Iron and Steel Technology, Peking.

[1] Hopei Museum, "The Shang dynasty site at Tai-hsi-tsun, Kao-ch'eng County, Hopei Province," *Kaogu* (*Archaeology*) (1973), no. 5, pp. 266–271.

[2] *Ibid.*, p. 270.

unearthed in China to date contains little nickel. Suggestions have, therefore, been made (e.g. by Prof. Hsia Nai of the Institute of Archaeology, Chinese Academy of Social Science) that the iron blade of the bronze axe might have been made of an iron meteorite. At the request of the Hopei Commission for the Preservation of Ancient Monuments, we have reexamined the blade to identify the material of which the blade was made, starting with preliminary results obtained by the Institute of Iron and Steel Research[3] and the Institute of Geology, Academia Sinica. Most of the electron microprobe analysis, metallography and X-ray analysis were undertaken by T. Y. Wu, W. H. Shih, T. Y. Lin, T. S. Tung, and C. Chao. Assistance has also been rendered by the Institute of Mining and Metallurgical Research, the Institute of Chemical Engineering in Metallurgy, and the Institute of Geology, which also provided meteorite specimens.

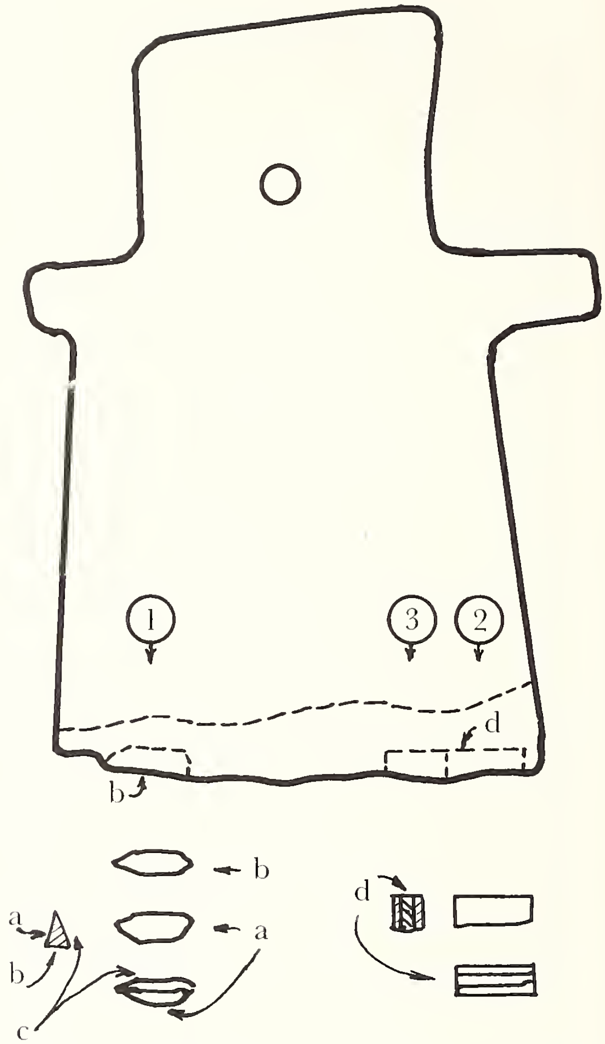

Fig. 2.—Sampling diagram. 1. Sample examined by the Institute of Iron and Steel Research. a. Surface shown in Fig. 4-1 (500 ×), ref. 2. b. Surface shown in Fig. 4-2 (50 ×), ref. 2. 2. Specimen studied by the Institute of Geology. d. Cross section examined in the present study. 3. Sample analyzed by the Institute of Geology.

IDENTIFICATION METHODS

Previous analyses[4] of the surface rust of this iron blade were done on a specimen obtained from spot 1 as shown in Figure 2. Particles of silicon-bearing materials and irregular stringers of calcium-bearing materials were found on a polished section near the surface. The prismatic sample, triangular in cross section, measures about 10 mm in length, 4 mm in height and 3 mm in width. It was easily detached from the oxidized blade and consists of 9–10 layers. Figure 4 (Right, 50 ×) of the original report was taken from the base and Figure 4 (Left, 500 ×) from one side of the triangle (marked b and a respectively in fig. 2). On the surface of the other side (c) are specks of green copper deposit resembling malachite, indicating that the sample was originally cracked, and its surfaces had been exposed to the environment. A specimen taken from the inside of the iron blade (spot 3 in fig. 2) was analyzed by the Institute of Geology with the following results:

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[3] *Ibid.*, p. 270.

[4] *Ibid.*, p. 270.

Spectrographic analysis: $Ge > 0.01$, $Co \gg 0.01$, $Cu > 0.01$, $Mg < 0.001$, $Ni > 0.4$, $Sn \simeq 0.01$, $Si \simeq 0.1\%$.

Chemical analysis:

	Rust Sample	Percentage of metallic contents in the original metal		
Fe_2O_3	68.74%	Fe	80.3	91.1%
FeO	7.84	Fe	10.8	
CoO	0.24	Co		0.4
NiO	2.5	Ni		3.4
CuO	10			
P_2O_5	0.65			

Judging by the X-ray diffraction analysis, the iron rust is mainly composed of limonite ($Fe_2O_3 . H_2O$) with some hematite (Fe_2O_3) and a small amount of magnetite (Fe_3O_4). The balance of the percentage figures shown in the above analysis is believed to represent the water in the limonite. Copper is thought to have come from the copper layer (see below and fig. 21) and to be contamination. Phosphorus originated from the raw material or contamination. No phosphides were observed. The equivalent metallic contents calculated from the chemical analysis of the rust sample are also listed in the above table. Since the rust is mainly composed of ferric oxide, part of the original NiO and CoO were lost as a result of weathering; the figures thus obtained are probably lower than their actual contents in the iron blade.

In view of the total oxidation of the iron blade, metallographic techniques or chemical analysis are insufficient for a definite identification of its origin. One can only compare the basic characteristics of the ancient man-made iron (pig iron and wrought iron) with that of the iron meteorite. Difference in composition, however, cannot serve as a major criterion. For example, in ancient times, charcoal was used to reduce iron ores that contained little sulfur and phosphorus, and the sulfur and phosphorus contents are low in man-made iron. Carbon exists in both man-made iron and iron meteorite; it can also be picked up during the iron-working process in addition to existing in carbonate deposits. Attention is, therefore, paid mainly to the analysis of inclusions and the distribution of nickel and cobalt in the rust of the iron blade, the two main features which can distinguish the oxidation products of meteoritic iron from man-made iron.

Characteristics of Man-Made Iron

Prior to the Warring States Period (fifth to third century B.C.) Chinese wrought iron articles were made from iron by the direct reduction process, and most of the siliceous slag was expelled by hammering.[5] Since the iron never went through a liquid state, inclusions formed by the impurities and FeO could not be removed completely, and the iron contains inclusions of various sizes of FeO and calcium-bearing fayalite. With the exception of the bronze *yüeh*-axe with iron blade, early wrought iron objects unearthed in China contain about 10% of such inclusions by volume. An example is the iron bar of the Spring and Autumn Period (eighth to fifth century B.C.) unearthed at Ch'eng-ch'iao in Liu-he, Kiangsu Province.[6] The late War-

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[5] Li Chung, "The development of iron and steel technology in Ancient China," *Kaogu Xuebao* (*Acta Archaeologica Sinica*) (1975), no. 2, pp. 1–22.

[6] Nanking Museum, "Excavation of the Eastern Chou tomb No. 2 at Ch'eng-ch'iao, Liu-he County, Kiangsu Province," *Kaogu* (1974), no. 2, 116–120.

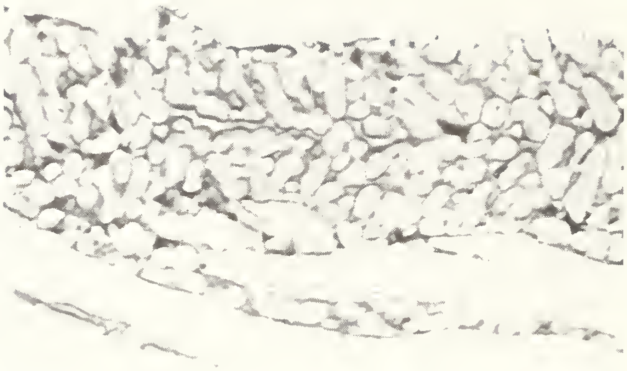

FIG. 3.—Scanning electron micrograph showing wustite-fayalite inclusions in the iron bar unearthed at Tomb No. 2, Liu-he, Che’ng-ch’iao, Kiangsu (ca. 500 B.C.). 275 × .

ring States swords and other iron weapons unearthed at the Lower Capital of the State of Yen, Hopei Province[7] and the steel swords and knives unearthed from the Tomb of Liu Sheng of middle Western Han Dynasty (113 B.C.) at Man-ch’eng, Hopei Province, all contain a large amount of such inclusions. Figure 3 shows the inclusions in the iron bar unearthed at Ch’eng-ch’iao in Liu-he, Kiangsu. The white particles in the inclusion are wustite (FeO) surrounded by the darker fayalite, which contains a small amount of calcium (fig. 4).[8] Figure 5 shows the structure and inclusions of the steel sword unearthed from the Tomb of Liu Sheng.

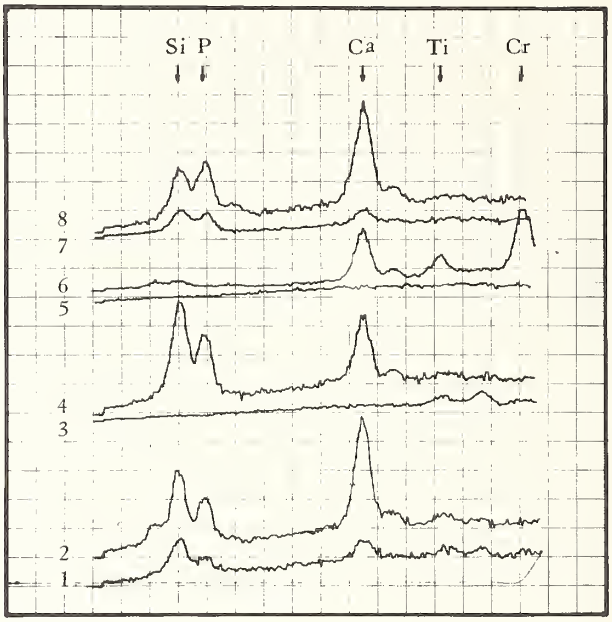

FIG. 4.—X-ray energy spectra of wustite (curves 3 & 5) and fayalite (curves 1,2,4,6,7, & 8) in the inclusion shown in Figure 3.

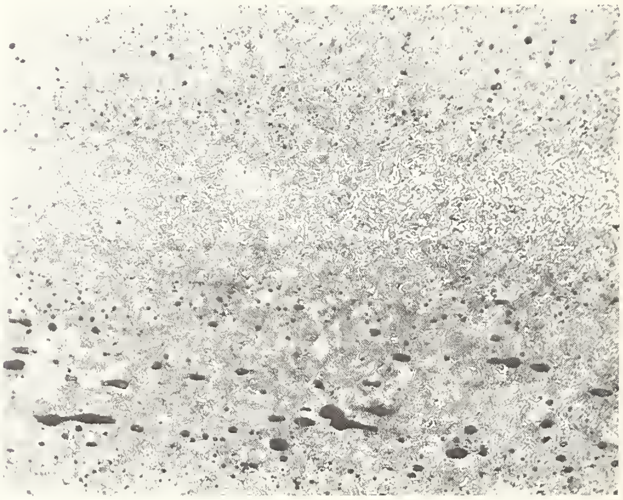

FIG. 5.—Inhomogeneities in carbon content and inclusions in Man-ch’eng steel sword made of cementated iron from a direct process (113 B.C.). 180 × .

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[7] Hopei Museum, “Excavation of tomb No. 44 at Yen-hsia-tu in Yi-hsian, Hopei Province,” *Kaogu* (1975), no. 4, pp. 228–240; also Peking Institute of Iron and Steel Technology, “Metallographic investigations on the iron artifacts from tomb No. 44 at Yen-hsia-tu in Yi-hsian,” *Kaogu* (1975), no. 4, pp. 241–243.

[8] Details to be published. Figure 4, deleted in the original Chinese text, is a reproduction of the original record of non-dispersive electron microprobe analysis, similar to Figures 44 and 45, of the inclusion shown in Figure 3. Curves 3 and 5 are for wustite, the others for fayalite.

Around the end of the Western Han and the beginning of the Eastern Han, which was about the beginning of the Christian era, the Chinese working people invented a steel-making process in which pig iron[9] was melted and puddled to remove carbon. The steel and wrought iron made by this process also contain numerous dispersed silicate inclusions. Though pig iron contains fewer inclusions, there is still a large number of minute but readily observable silicon-bearing inclusions (see fig. 25). By contrast, as the cooling rate of an iron meteorite is extremely low during its formation, any sulfide, phosphide or silicate inclusions are usually present in large crystals and the iron-nickel matrix contains only very few inclusions. For this reason, a search for the existence and the distribution of the inclusions provides a useful means to identify the origin of the material. While it is difficult to distinguish the original FeO inclusions from the FeO which has formed in the rust, man-made iron can still be distinguished from meteoritic iron by examining the optical properties of the silicate inclusions. The use of electron probe microanalysis (EPMA) can easily identify the presence of elements other than iron, such as the silicon in inclusions. The electron microprobe is an instrument which focuses an electron beam on to a solid surface, producing X-rays from a very small region (10^{-4} to 10^{-1} mm) for compositional analysis. Electrons emitted from the electron gun pass through magnetic lenses in vacuum and are focused on the selected area of the sample. Upon electron bombardment, each element composing the sample will excite its own characteristic X-rays, and one can identify each element and its quantity through X-ray wave-length or energy measurements. The search for silicon-bearing inclusions by electron microprobe analysis and the metallography in the iron blade of the *yüeh*-axe are important means in the identification of its origin.

The electron microprobe may be further used to determine the distribution of nickel, cobalt and other elements in the blade. The presence of characteristics that are never found in man-made alloys but exclusively in iron meteorites would provide an important criterion in the identification of its origin.

Characterisitics of Iron Meteorites

There are two different kinds of meteorites, stony meteorites and iron meteorites. The latter consist mainly of iron-nickel alloys with the following compositions.[10,11]

Ni	4–20%	(great majority 5–10%)
Co	0.3–1.0%	(majority 0.4–0.5%)
Cu	0.01–0.05%	
P	0.01–1.2%	(majority 0.1–0.3%)
S	0.001–0.6%	(majority 0.2–0.6%)
C	0.006–0.2%	(majority 0.01–0.2%)

A few iron meteorites may have 23–34% of nickel content, sometimes perhaps containing even as much as 60%.[12] But there are also cases in which the nickel content is less than 4%.[13] Traces of germanium and gallium are

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[9] Recent investigations show that cast iron had been discovered before, and was widely used after, the 6th century B.C. in China.

[10] C. B. Moore, C. F. Lewis and D. Nava, "Superior analyses of iron meteorites," *Meteorite Research*, Proceedings of a symposium on meteorite research, Vienna, August 7–13, 1968. (New York: Springer-Verlag, 1969), pp. 738–748.

[11] H. J. Axon, "Metallurgy of meteorites," *Progress in Materials Science*, vol. 13 (1968), pp. 183–228.

[12] Oyang Chi-yuan, Tong Wu and Chou Ching-liang, "Mineralogical studies of three iron meteorites (from Shangtu, Nan-tan and Liang-cheng)," *Scientia Geologic Sinica*, no. 3 (1964), pp. 241–258.

[13] H. H. Coghlan, *Notes on Prehistoric and Early Iron in the Old World* (Oxford, 1956), p. 27.

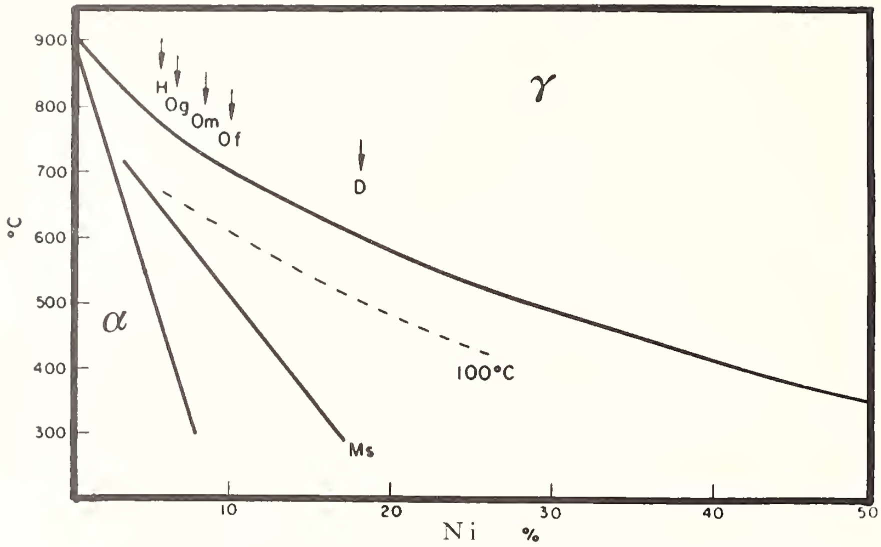

Fig. 6.—Iron-nickel phase diagram below 900°C. After E. A. Owen and Y. H. Liu, "Further X-ray study of the equilibrium diagram of the iron-nickel system," *Journal of the Iron and Steel Institute*, vol. 163 (1949), pp. 132–137.

also present in iron meteorites. An examination of eighty-eight pieces of iron meteorites show that their germanium and gallium contents may be divided into the following four groups.[14]

	Gallium ($\times 10^{-6}$ ppm)	Germanium ($\times 10^{-6}$ ppm)
I	80–100	300–420
II	40–65	130–230
III	8–24	15–80
IV	1–3	1–1

The meteorite cooled very slowly from a high temperature during its formation; its cooling and transformation might have taken as long as 4×10^9 years.[15] Its cooling rate in the solid state might be as low as 0.5–100°C per million years and the majority were in the range of 1–10°C/m.y. The troilite and graphite precipitated from the liquid state, and the troilite, rhabdite and cohenite precipitated from the solid state are quite different from inclusions in a man-made alloy. They are much larger in the iron meteorite, and measure from a few millimeters to a few centimeters. However, there are very few inclusions in the rest of the iron meteorite. Iron meteorites are usually characterized by a Widmanstätten structure, formed during their extremely slow cooling in accordance with the iron-nickel equilibrium phase diagram (fig. 6).

The diagram shows the particular phases (and corresponding compositions) which coexist in equilibrium at a given temperature. In Figure 6, composition (in terms of the percentage of nickel) forms the abcissa, and temperature the ordinate. As 900°C is well below the melting point of any iron-nickel alloy, the portion of the diagram reproduced here is solely concerned with transformations in the solid state. The area above the upmost curve is a region occupied by nickel-rich γ-phase (taenite). The area under the lowest curve is the region of α-phase (kamacite). The area between these two extreme curves is the region where γ-phase and α-phase co-exist (plessite). At a given temperature, the nickel contents of α-phase and γ-phase correspond to the two intersections of the isothermal line and the equilibrium curves. When γ-phase coexists with α-phase, the former becomes enriched in nickel. The latter phenomenon is due to the mutual solubility of γ-iron and nickel, which in turn is the result of their having an identical crystal structure and similar atomic sizes. Above 770°C, the alloy with composition H (hexahedrite) is γ-phase. Upon cooling to 770°C, the α-phase which contains about 2% of nickel is precipitated while the excess nickel diffuses toward the γ-phase. As cooling proceeds, the α-phase grows continuously with a gradual increase in the nickel content at the expense of γ-phase (its nickel content also keeps increasing). When the temperature is lowered to about 500°C, γ-phase is transformed completely to α-phase with the composition represented by H. The nickel distribution in the α-phase is generally uniform. When such an iron meteorite fractures, the fracture path follows hexahedral cleavage, hence the term hexahedrite. As the hexahedrite impinges on the air or earth, twins will form as a result of rapid deformation of the α-iron. The twins so formed are called the Neumann bands, which are independent of the alloy composition. For the same reason, the Neumann bands can also be seen in the α-phase in the higher nickel iron meteorites. Figure 7 shows the twins in the α-phase of the giant iron meteorite (Armanty), which weighs about 20 tons and has an average nickel content of 9.92%, found in the Dzungaria Basin, Sinkiang Uighur Autonomous Region.[16]

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[14] J. F. Lovering, W. Nichiporuk, A. Chodos and H. Brown, "The distribution of gallium, germanium, cobalt, chromium and copper in iron and stony-iron meteorites in relation to nickel content and structure," *Geochimica et Cosmochimica Acta*, vol. 11 (1957), pp. 263–278.

[15] E. Anders, "Origin, age and composition of meteorites," *Space Science Reviews*, vol. 3, (1964), pp. 583–714.

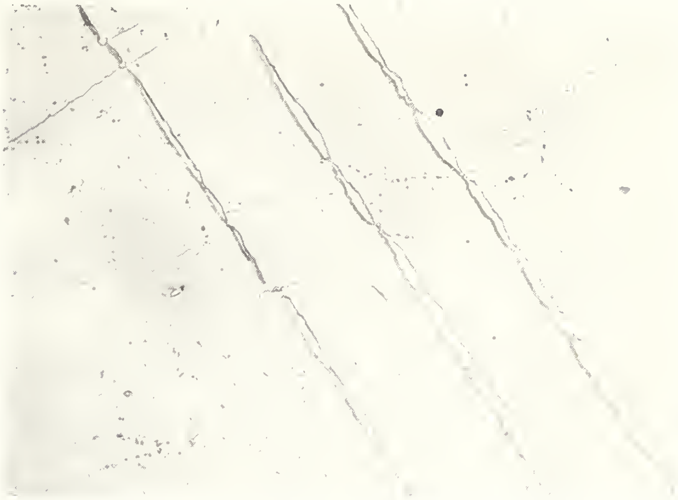

FIG. 7.—Deformation twins (Neumann bands) in kamacite in the iron meteorite (Armanty) found in Dzungaria, Sinkiang. 200 ×.

In the case of a meteorite with a higher nickel content, the α-phase starts to precipitate at a lower temperature. As the temperature cools below 450°C, the diffusion of nickel becomes too sluggish, the α-phase ceases to grow, and a part of the γ-phase is retained. The α-phase always precipitates along certain crystallographic planes of the original γ-phase. There are four equivalent planes corresponding to the faces of an octahedron. The structure thus obtained is called a Widmanstätten structure and this type of meteorite is called an octahedrite, represented by

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[16] Oyang Chi-yuan and Tong Wu, "Chemical composition, mineralogical and structural studies of three iron meteorites of China (from Dzungaria, Ujumqin and Feng-chien)," *Scientia Geologica Sinica*, no. 2 (1965), pp. 182–192. Editor's note: This meteorite is catalogued as the Armanty meteorite, Outer Mongolia, ca. 47°N, 88°E. See M. H. Hey, *Catalogue of Meteorites*, London, British Museum (Natural History), Publication No. 464, 3rd ed., 1966, p. 27.

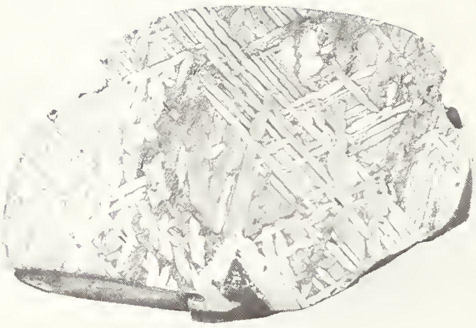

Fig. 8.—Widmanstätten structure of the Dzungarian (Armanty) meteorite; 1.1 ×.

the symbol O. Figures 8 and 9 show the Widmanstätten structures of the iron meteorite (Armanty) found in the Dzungaria Basin. On the basis of the respective widths of the α-phase in their Widmanstätten structures, iron meteorites are designated as O_g (>1.5 mm), O_m (0.5 – 1.5 mm), O_f (0.2 – 0.5 mm), O_{ff} (<0.2 mm). The lowest nickel content of a meteorite in which taenite is present is about 5.7%[17] while most iron meteorites contain about 8% nickel.[18,19] Figure 10 shows the frequency of occurrence of various nickel contents (abscissa) and the corresponding widths of α-phase plates (ordinate) in 236 iron meteorites, accounting for about one half of the known iron meteorites. It can be seen that most of the iron meteorites have a nickel content of about 7.0–9.5% with an α-phase width of about 0.5–1.5 mm, i.e., O_m type. Under an extremely slow cooling condition, an iron-nickel alloy with 8% nickel will precipitate at 730°C an α-phase that contains 2% nickel. (It has been suggested that taenite

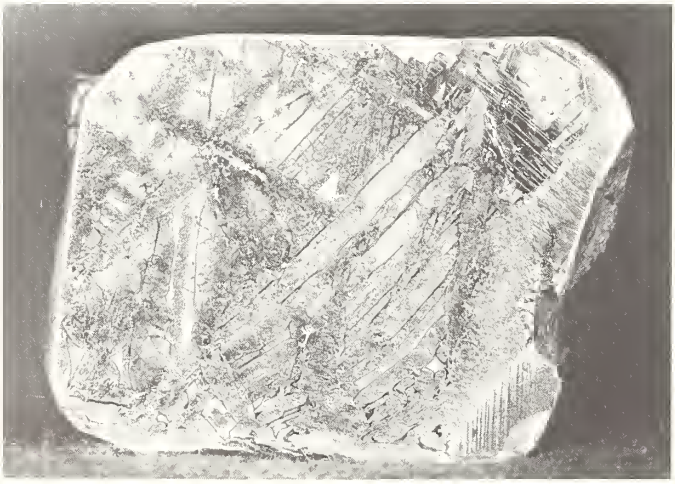

Fig. 9.—Widmanstätten structure of the Dzungarian (Armanty) meteorite; 3.2 ×.

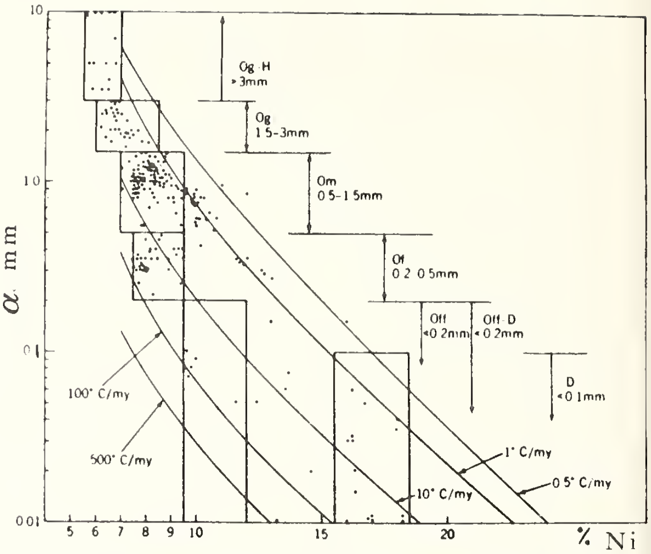

Fig. 10.—Correlation between kamacite width (mm) and nickel content of 236 iron meteorites. Each point represents one iron meteorite, m.y. represents million years. After Goldstein.[19]

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[17] E. P. Henderson and S. H. Perry, "A discussion of the densities of iron meteorites," *Geochimica et Cosmochimica Acta*, vol. 6 (1954), pp. 221–240.

[18] Oyang and Tong, "Chemical composition . . ."

[19] J. I. Goldstein, "The classification of iron meteorites," *Meteorite Research*, Proceeding of a symposium on meteorite research, Vienna, August 7–13, 1968. (New York: Springer-Verlag, 1969) pp. 721–737.

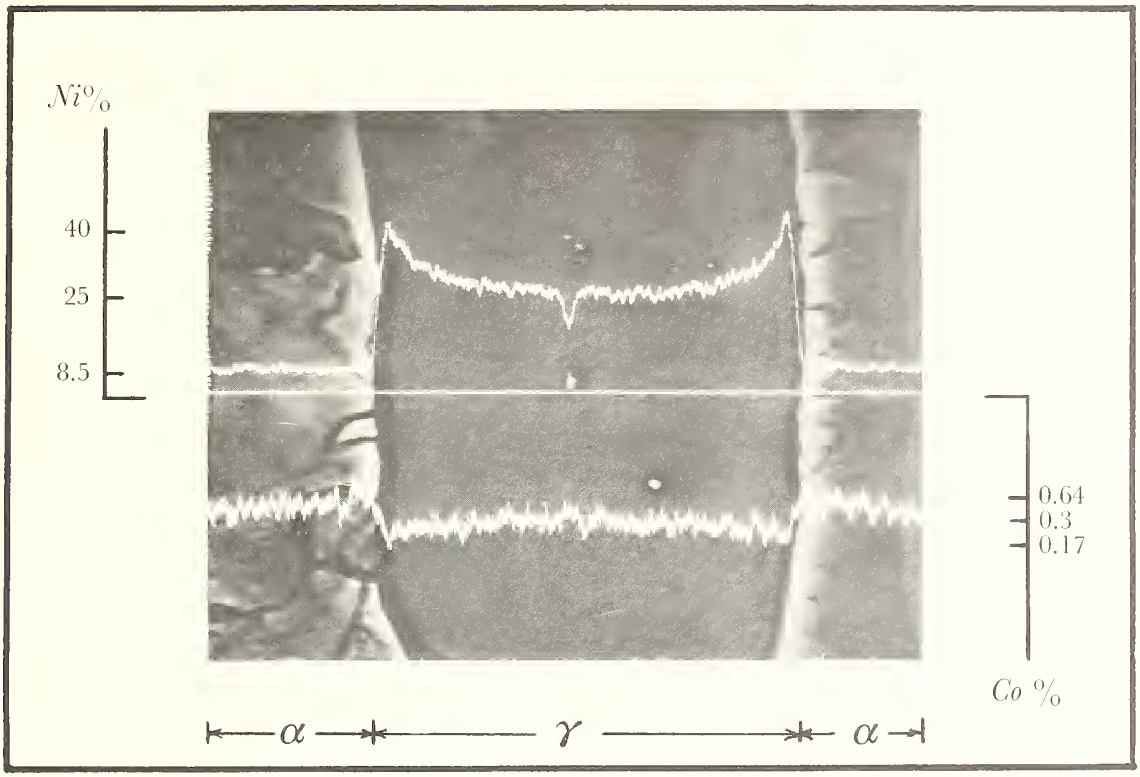

FIG. 11.—Nickel and cobalt distributions in the Dzungarian (Armanty) meteorite. 750×.

undergoes 100°C undercooling before any decomposition, as represented by the broken line in Figure 6). The excess of nickel diffuses into the γ-iron. As cooling continues, the amount of the α-phase and the nickel contents in both phases keep increasing. At about 450°C, the transformation process ceases as a result of the slow diffusion of nickel in the γ-phase. At this point, the average nickel content in the α-phase is 5.2%.[20] Upon diffusing into the γ-phase, part of the nickel will segregate in the vicinity of the α/γ interface, forming a nickel rich layer with a nickel content of over 38%. The cobalt moves in a direction opposite to that of the nickel. Figure 11 shows a two-phase region of the Dzungarian (Armanty) iron meteorite (fig. 9) with the γ-phase, about 75 microns wide in the middle. EMPA scans of the composition along the central white line are superimposed on the figure, the upper and the lower curves representing respectively the variations in the nickel and cobalt contents. Figure 12 represents the nickel and cobalt distributions (the upper thick line represents nickel while the lower thin line represents cobalt) of another region with a wider γ-phase (120 microns). It is clear from these figures that the nickel segregated to the γ-phase with the maximum nickel content located in the

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[20] The nickel content in the α-phase is actually a little higher. In meteorites with 8–12% nickel, the average nickel content in the α-phase is 7.27%. It ranges from 7.0 to 8.5% in the Dzungarian (Armanty) meteorite. The minimum nickel content in the α-phase in meteorites containing 5.6–6.9% nickel is 6.4%. See S.J.B. Read, "Electron probe microanalysis of the metallic phases in iron meteorites," *Geochimica et Cosmochimica Acta*, vol. 29 (1965), pp. 535–549.

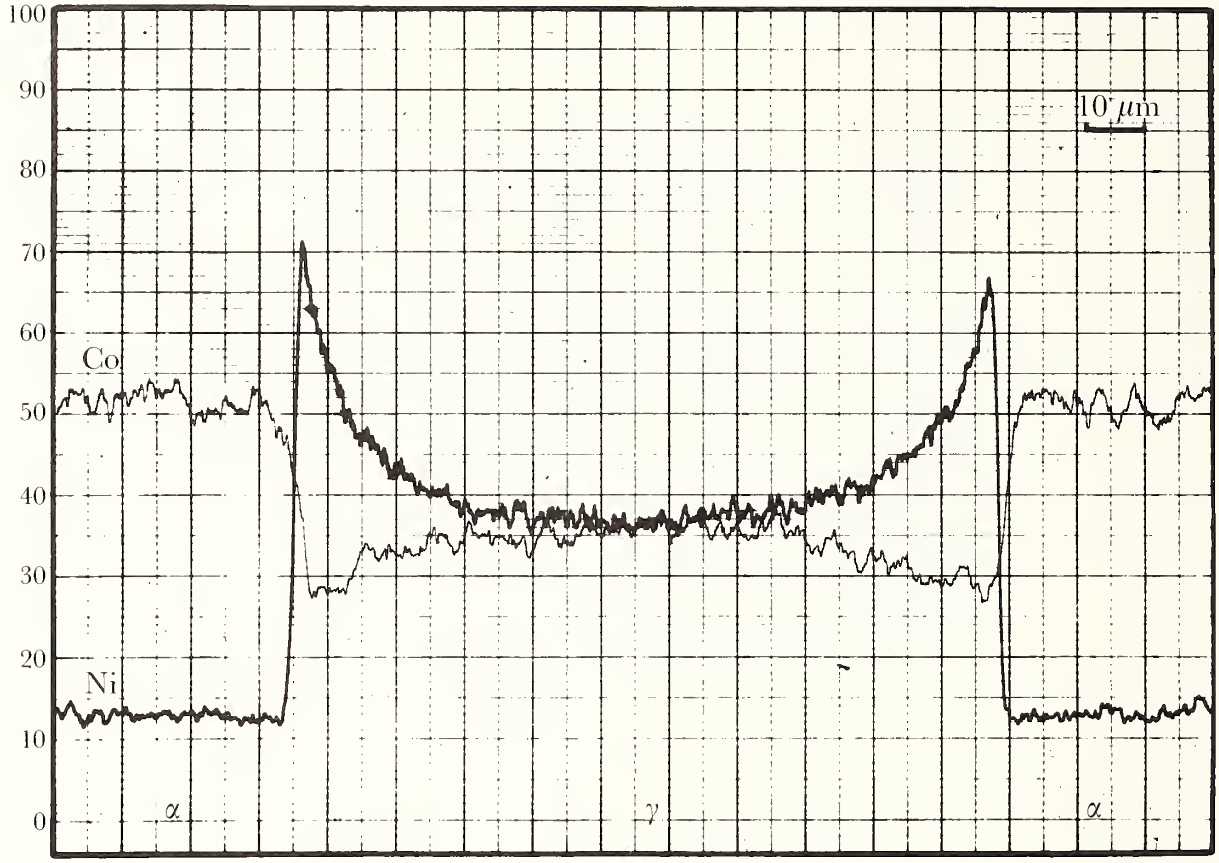

Fig. 12.—Nickel and cobalt distributions from a region different from Figure 11, in the Dzungarian (Armanty) meteorite.

vicinity of α-phase, while the cobalt segregated to the α-phase with the minimum cobalt content located in the γ-phase near α/γ interface. All these suggest that the α-phase is the growing phase, the growth of which is limited by the diffusion rate of the alloy elements. The metal contents measured at various points shown in the two figures are as follows:

		α-phase	γ-phase (near α/γ interface)	γ-phase
Figure 11	Ni%	8.5	40	25
	Co%	0.64	0.17	0.3
Figure 12	Ni%	7.0	33	18
	Co%	0.6	0.2	0.4

Since the α-phase normally exists in plates, the higher nickel γ-phase and high nickel layer are also in the layer form, though a rod-like kamacite region (particle-like in a metallographic section) has been observed in the Dzungarian (Armanty) meteorite.

Sometimes the low nickel region of the γ-phase will precipitate continuously a fine layer-like or rod-like α-phase at low temperature, as shown in Figure 13. The γ-phase in the vicinity of the α/γ interface has a higher nickel content, hence is more stable and retained at room temperature. The middle region with its lower nickel content has further precipitated α-phase with part of the γ-phase retained as shown in Figure 14. Figure 15 is a corresponding X-ray scan of the same area, with the bright areas representing

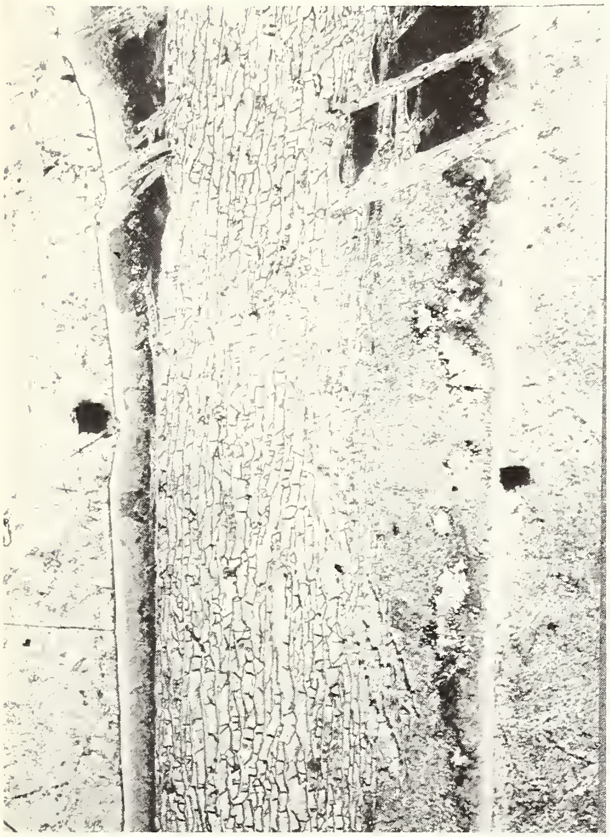

FIG. 13.—α–γ structure of kamacite-taenite in the Dzungarian meteorite. 43 × .

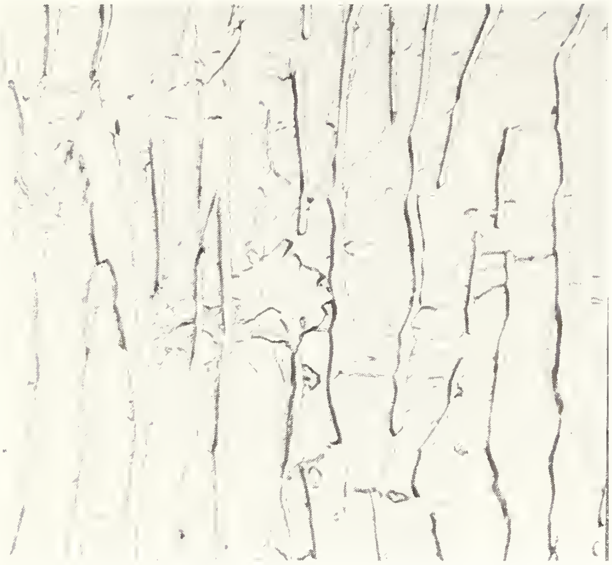

FIG. 14.—α–γ (kamacite-taenite) in the Dzungarian (Armanty) meteorite, 270 × .

the high nickel regions. Figure 16 shows the secondary electron image from a similar region. Figures 17 and 18 are "Aeroview" images that represent, respectively, the nickel and cobalt distributions in this region. The Aeroview is composed of a number of EMPA line scans similar to those shown in Figures 11 and 12. The baseline of each scan corresponds to the scan trace on the sample (fig. 16). The vertical distance above the baseline represents the nickel or cobalt content in each scan. Hence the ridges in these two figures correspond to the high Ni(Co) regions while the valleys correspond to the low Ni(Co) regions. Figures 17 and 18 demonstrate the lamellar structure that results from the segregation of the nickel to the γ-phase and of the cobalt to the α-phase. Since the diffusion rate of nickel in the γ-phase increases at higher temperatures, the nickel segregation seen here must have taken place at low temperatures

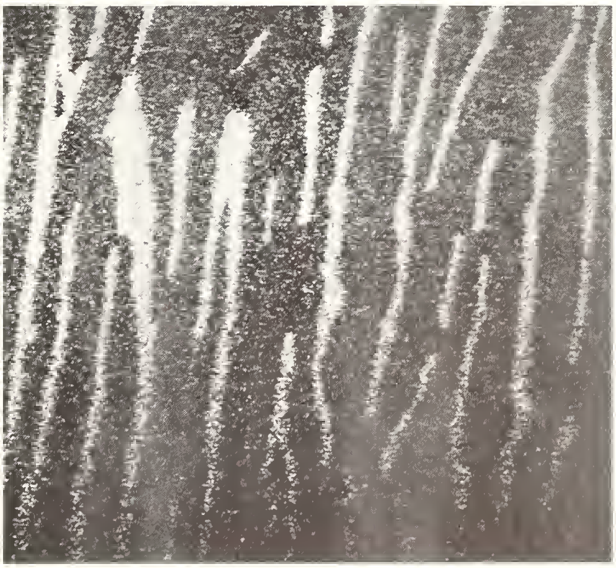

FIG. 15.—Nickel X-ray scan image of the area shown in Figure 14.

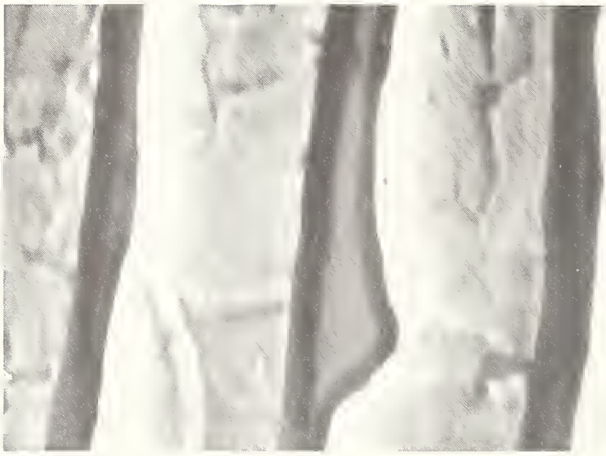

FIG. 16.—Secondary electron image of the α–γ structure (kamacite-taenite) in the same specimen as Figure 14. 1600 × .

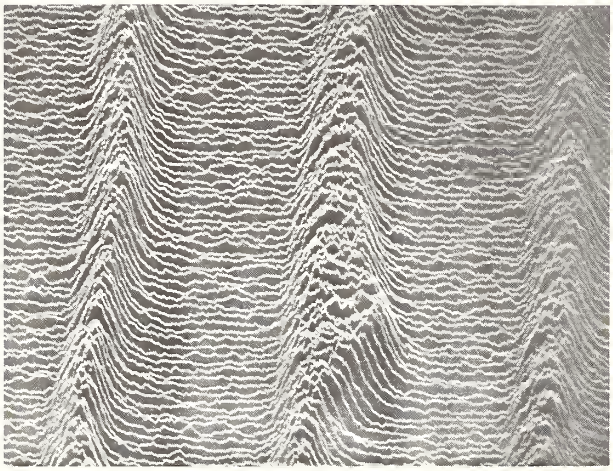

FIG. 17.—Aeroview of nickel distribution in the α–γ structure in the same area as Figure 16.

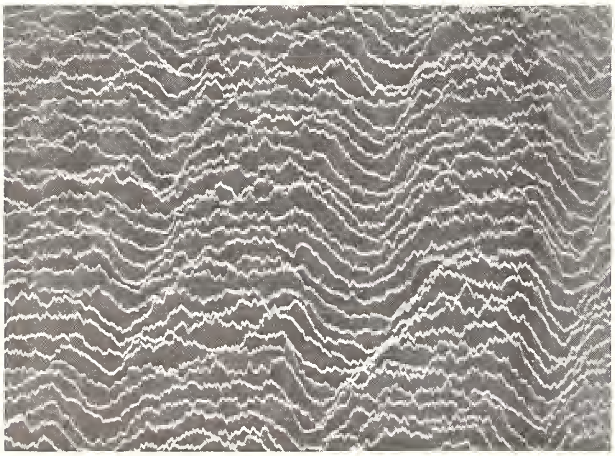

FIG. 18.—Aeroview of cobalt distribution in the α–γ structure in the same area as Figure 16.

and over a long period of time, i.e. with an extremely low cooling rate. From observation of a large number of iron meteorite specimens, the cooling rate has been found to be in the range of 1–10°C/m.y. for meteorites with a nickel content of about 8% (fig. 10).

When iron-nickel alloys are cooled under laboratory conditions, γ-iron does not decompose into $\alpha + \gamma$. Even under the slowest cooling conditions, the γ-iron will remain undecomposed down to a certain temperature (which corresponds to the Ms line in Figure 6), then transforms diffusionlessly into martensite.[21,22] Only when the martensite is reheated can it decompose into two phases,[23] as the nickel has a higher diffusion rate in the martensite. Even so, it takes a very long time for this reaction to occur. For example, when Fe-Ni martensite with a nickel content of 7.4% is reheated to 670°C, it takes 100 hours to produce blocky α-phase with slight nickel segregation. The lower the nickel content, the longer it takes to complete this transformation. The nickel distribution of a nickel steel with 3% nickel at a temperature where both α-phase and γ-phase co-exist has been reported by Aaronson *et al.*[24] When a 0.11% C, 3.28% Ni steel was heated to the γ-phase region, and then cooled to and held at 734°C for 811,900 seconds (9.4 days), α-phase was precipitated. Subsequent quenching transformed the residual γ-phase into a matrix of acicular martensite. These features are shown in Figure 19 with the short arrow pointing to the α-phase. Figure 20 shows the nickel content, as determined by microprobe analysis, along the long arrows (a) and (b) in Figure 19. The nickel content drops slightly in the α-phase while it increases in the γ-phase. There is only a 2% difference between the maximum and minimum values with a ratio of 1.8 between nickel contents in γ and in α. When the sample was quenched and then tempered at 734°C in order to speed up the transformation, the result obtained (fig. 8 in Aaronson

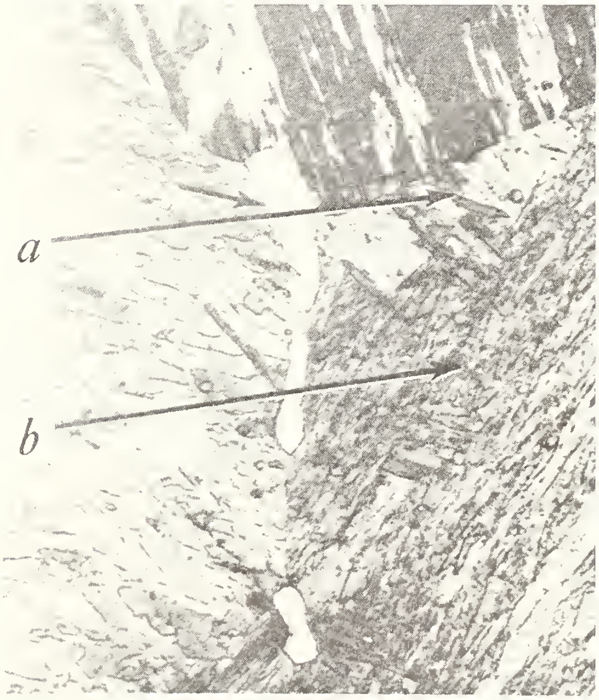

Fig. 19.—α-phase (short arrow) precipitated in 3.28% Ni steel at 734 C after holding for 811,900 seconds. The nickel distribution along arrows a and b are shown in Figure 20. From Aaronson and Domian.[24]

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[21] F. W. Jones and W. I. Pumphrey, "Free energy and metastable states in the iron-nickel and iron-manganese systems," *Journal of the Iron and Steel Institute*, vol. 163 (1949), pp. 121–131.

[22] A. Gilbert and W. S. Owen, "Diffusionless transformation in iron-nickel, iron-chromium and iron-silicon alloys," *Acta Metallurgica*, vol. 10 (1962), pp. 45–54.

[23] N. P. Allen and C. C. Early, "The transformations α—γ and γ—α in iron-rich binary iron-nickel alloys," *Journal of the Iron and Steel Institute*, vol. 166 (1950), pp. 281–288.

[24] H. I. Aaronson and H. A. Domian, "Partition of alloying elements between austenite and pro-eutectoid ferrite and bainite," *Transactions of the Metallurgical Society, A.I.M.E.*, vol. 236 (1966), pp. 781–796.

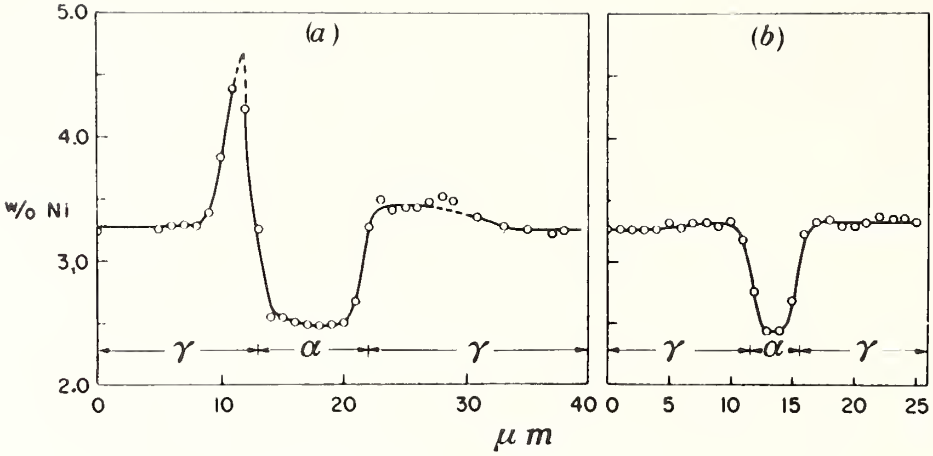

FIG. 20.—Line analyses of nickel along arrows a and b in Figure 19. From Aaronson and Domian.[24]

et al.) after tempering for 817,560 seconds (9.5 days) was similar to that obtained from annealing. Even if the concentration ratio was reduced to 1.3, it still required 11 hrs. for a diffusion distance of 5 microns. As the diffusion time is proportional to the square of the diffusion distance, much longer time would be required for the larger diffusion distance as observed in a meteorite. Although in higher nickel alloys a higher distribution ratio is possible which would facilitate diffusion, more time is still required as the transformation takes place at a much lower temperature. According to the nickel diffusion rate in the γ-phase and its temperature dependence,[25] it takes 20 and 1500 times longer to cover the same diffusion distance if the temperature is dropped from 730°C to 650°C and 550°C respectively. Furthermore, since the α-phase grows rapidly at a lower temperature (below 700°C), nickel cannot redistribute itself among the α-phase and the γ-phase. In the case of an iron meteorite, it has been estimated that it requires 8.8×10^4 years and 1.3×10^5 years[26] to give an even distribution of nickel in a 2.0 mm α-phase and a 0.07 mm γ-phase at 600°C respectively. Hence it is practically impossible to obtain an artificial high-nickel layer in a nickel-bearing iron alloy.

Therefore, an examination of the nickel distribution and its variation in the iron blade of the *yüeh*-axe will provide a reliable criterion for the identification of the raw material of the iron blade. Of course, the nickel distribution in hexahedrite meteorites is more uniform, and the nickel distribution in octahedrites tends to become uniform with hot working or long weathering. If we can detect in the remaining oxide of the iron blade any difference in nickel content and a lamellar nickel distribution beyond those obtainable in an artificial specimen, we can then positively establish that the iron blade was made from an iron meteorite.

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[25] K. Hirano, M. Cohen and B. L. Auerbach, "Diffusion of nickel into iron," *Acta Metallurgica*, vol. 9 (1961), pp. 440–445.

[26] H. C. Urey, "Diamonds, meteorites and the origin of the solar system," *Astrophysical Journal*, vol. 124 (1956), pp. 623–637.

EXPERIMENTAL RESULTS AND DISCUSSION

Structure of the Iron Blade

Figure 21 shows the microstructure of an unetched specimen (sectioned from spot 2 in fig. 2). Zone 1, the outermost areas, represents the bronze which shows no structure before etching. In Zone 2, dark gray tin-rich oxide (23–33% tin) shows up the dendritic structure of cast bronze. Zone 3 represents microfissures which still contain small amounts of copper oxide and malachite. Beyond these is Zone 4, which has a thickness of about 0.025–0.035 mm, and is composed of layers of various shades of gray. Its cast structure is still discernable from the distribution of light gray and dark gray oxides in a few areas, though the dark gray part gradually fades toward the border and finally merges with the light gray layer. The gray copper oxide layer contains only 0–0.5% tin. This shows that the bronze located near the iron oxide has been oxidized to Cu_2O, and the tin-rich area to SnO or SnO_2. But owing to the difference in crystal structure and in valence between SnO_2 and Cu_2O, SnO_2 could not be retained in the crystal lattice of Cu_2O and was gradually lost through weathering. Zone 5 is composed of iron oxide with lamellar structure as observed under polarized light. Within the iron oxide zone is a prominent layered band (Zone 6), composed of iron oxide (with nickel) and copper oxide (without nickel). Figure 22 is an electron micrograph of this band, while Figure 23 shows its copper distribution. When compared with Figure 21, these two figures also show that inter-diffusion of iron and copper takes place between Zone 5 and Zone 6. The diffusion must have occurred during casting, the band originally being composed of copper and iron metal, not of oxides. Moreover, there are light gray veins running from the copper-iron band into the

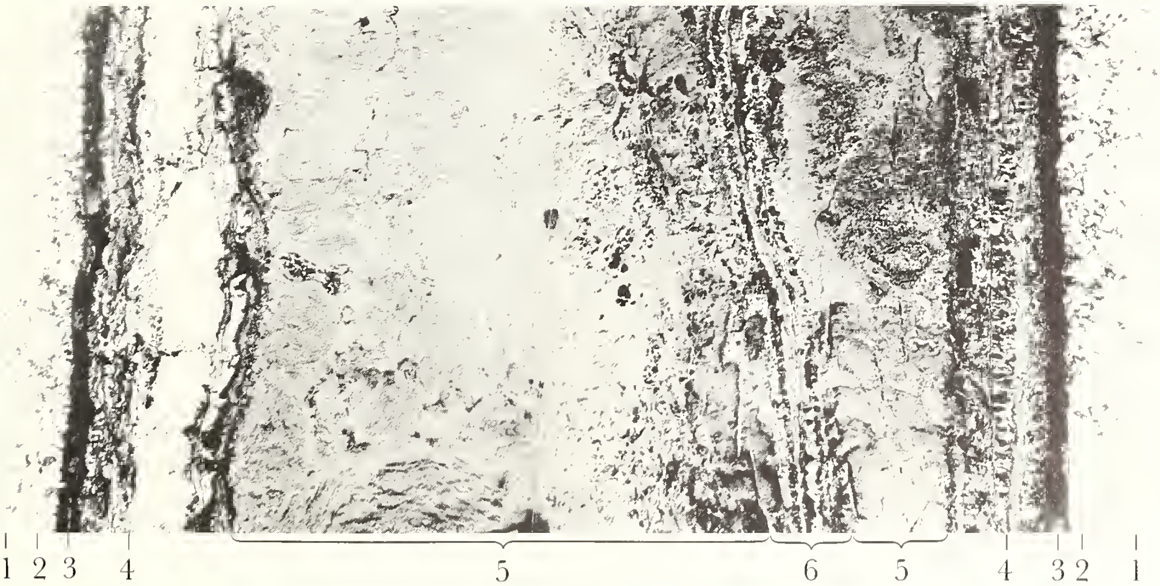

FIG. 21.—Metallograph of a cross section of the Kao-ch'eng *yüeh*-axe iron blade. Unetched. 50 ×

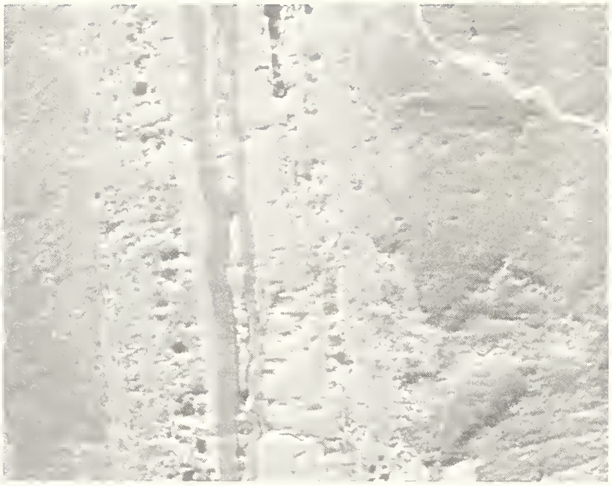

FIG. 22.—Electron micrograph of the copper bands (Zone 6 in Figure 21). 222 × .

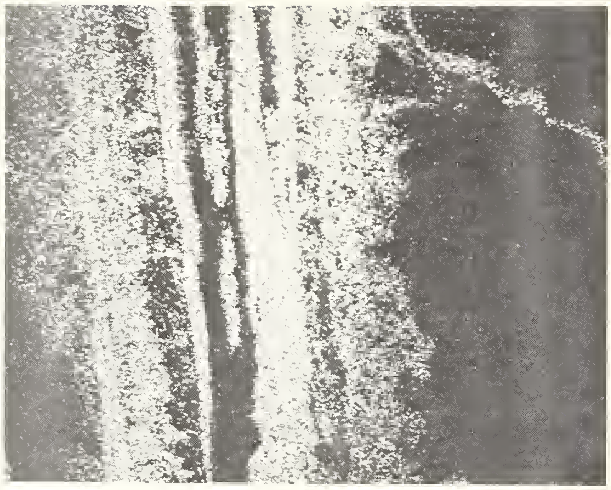

FIG. 23.—X-ray scan image showing the distribution of copper in the iron blade. 277 × .

iron rust. These veins are now composed of copper oxide as shown in Figure 23. We will refer to the copper-iron band and copper veins later in the paper.

The inclusions are examined by metallography and electron microprobe techniques. Silicate and other coarse inclusions were searched for at 600 × under reflected light and polarized light. No coarse inclusion has been found in the iron rust. Under crossed nicols, a few silicate inclusions with dark crosses are observed in bronze and copper oxide. The whole sample contains only 6 or 7 silicates, which are mostly located in the cast bronze. With the electron microprobe, the silicon X-ray scan (fig. 24) shows a single

FIG. 24.—X-ray scan image showing the distribution of silicon in the iron blade. 250 × .

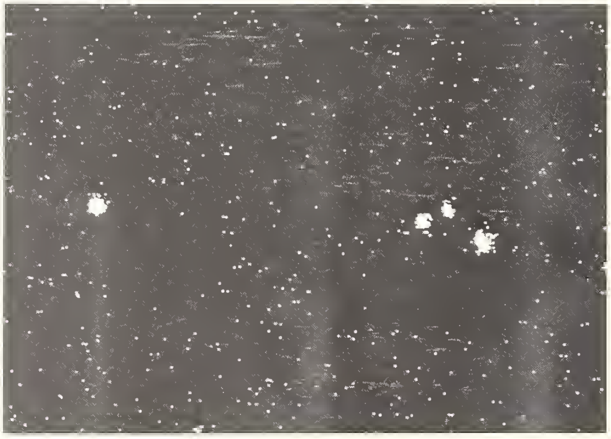

FIG. 25.—X-ray scan image showing the distribution of silicon in the Mien-ch'ih axe made of decarburized cast iron (before 6th century A.D.). 600 × .

particle in the iron rust, giving X-ray counts equivalent to about 1/30 of pure silicon. This shows that the presence of silicate can be detected by this means, and that the iron blade does not contain inclusions characteristic of man-made iron Figure 25 (600 ×) shows the distribution of silicon-bearing inclusions in a decarburized and annealed cast iron axe of the Six Dynasties (prior to the 6th century A.D.), unearthed at Mien-ch'ih, Honan. The number of inclusions in the figure would increase 5.5 times at 250 × . Ancient wrought iron contains an even larger number of inclusions. Figure 26 shows the distribution of inclusions in a steel sword (the microstructure of which is shown in fig. 5), unearthed from the tomb of Liu Sheng at Man-ch'eng. Figures 27 and 28 show respectively the distribution of silicon and calcium. Figures 29, 30, and 31 show respectively the electron micrograph, the silicon distribution and the calcium distribution in the iron rust of the sword. Figures 27 and 30 attest to the presence of numerous silicon-bearing inclusions in man-made iron even after long weathering. By comparing Figure 28 with Figure 31 one can see that the calcium content increases as a result of the oxidation of iron and contact with underground water, but its quantity varies with the structure of the iron rust.

The copper oxide and bronze have also been found to contain silicon-bearing inclusions. Electron microprobe analysis shows that an average of one or two silicon-bearing inclusions per 10 μm^2 may be observed inside these regions. It is believed that these inclusions were introduced during the melting and casting processes.

Observations of inclusions thus clearly reveal that the iron blade of the bronze *yüeh*-axe differs fundamentally from either man-made iron or pig-iron.

Chemical Composition and the Distribution of Nickel and Cobalt in the Iron Blade

Prior to the examination of nickel and cobalt contents and their distribution, the silicon, calcium, germanium and carbon contents in the iron blade were determined. Since the presence of silicon, carbon and calcium-bearing materials has been reported in a previous chemical analysis of a sample taken near the surface,[27] it is necessary to examine the quantities of these elements in the iron blade with a view to determine whether the surface has been contaminated by underground water through extended contact with the soil. Moreover, some iron meteorites contain germanium and gallium. The germanium segregation in the γ-phase is similar to that of nickel.[28] Hence, the presence of germanium was also sought. Its average concentration was obtained by using the microprobe with a 100-micron diameter electron beam.

Silicon. The silicon content in the iron blade is very low. Only a very low background is seen with Si X-ray scanning at 1000 × . With the iron axe (No. 257) unearthed at Mien-ch'ih, which has a silicon content of 0.16%, as a standard, the silicon content in the iron oxide of the iron blade is in the range of 0.03–0.05%.

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[27] Hopei Museum, "The Shang dynasty site . . . ," p. 270.

[28] W. Nichiporuk, "Variations in the content of nickel, gallium, germanium, cobalt, copper and chromium in the kamacite and taenite phases of iron meteorites," *Geochimica et Cosmochimica Acta*, vol. 13 (1958), pp. 233–247.

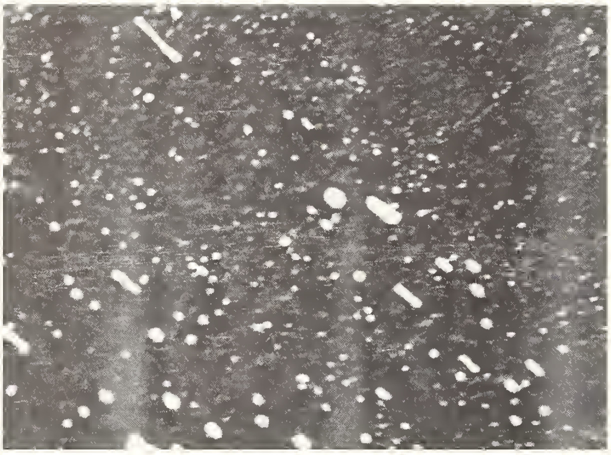

Fig. 26.—Inclusions in a Man-ch'eng steel sword from a Han tomb (113 B.C.) made of cementated iron by direct process. Reversed electron image. 250×.

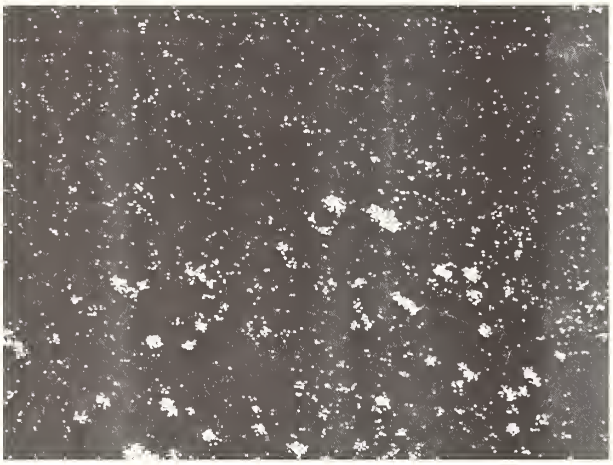

Fig. 27.—X-ray scan image showing the distribution of silicon in Figure 26.

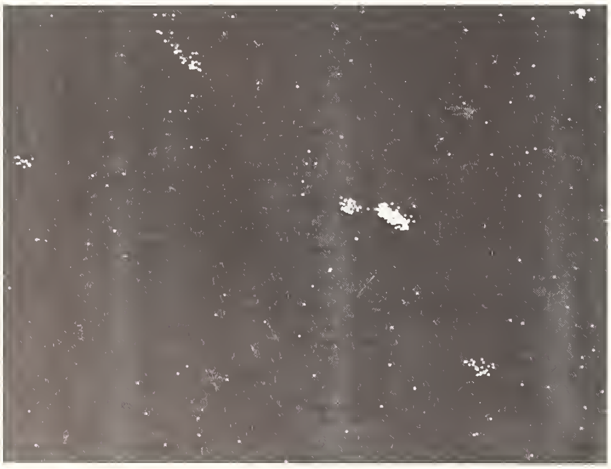

Fig. 28.—X-ray scan image showing the distribution of calcium in Figure 26.

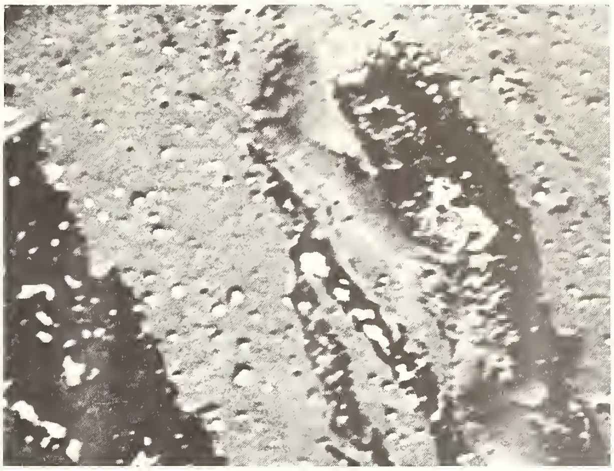

FIG. 29.—SEM image of the iron rust on the Man-ch'eng steel sword shown in Figures 5 and 26.

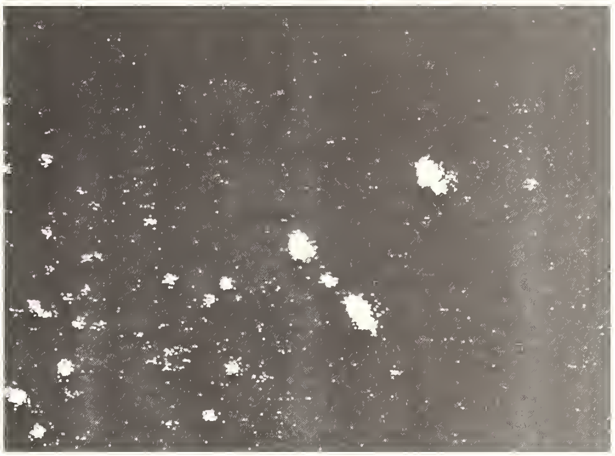

FIG. 30.—X-ray scan image showing the distribution of silicon in Figure 29.

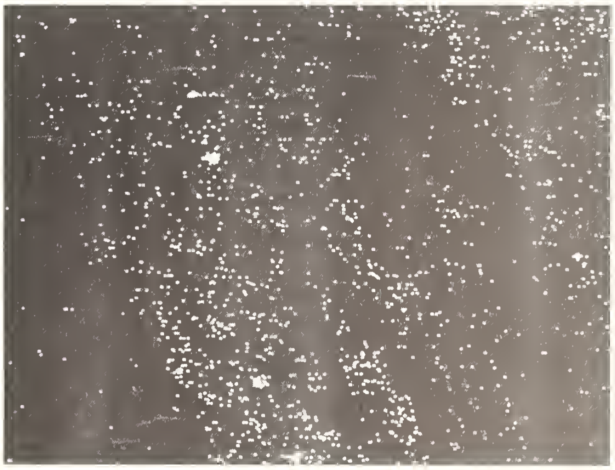

FIG. 31.—X-ray scan image showing the distribution of calcium in Figure 29.

Calcium. The calcium content in the iron blade is extremely low. The calcium distribution (fig. 28) obtained by Ca X-ray scanning is similar to that found in the metal matrix of the steel swords unearthed from the Han tomb at Man-ch'eng. It is much lower than the calcium content (fig. 31) found in the rust area of the sword which had been contaminated by soil and underground water. Nor are there any calcium-bearing inclusions. It is certain that the interior of the iron blade contains neither Ca nor Ca-bearing inclusions.

Germanium. The Ge X-ray count in the iron blade is slightly lower than that obtained from the steel swords unearthed from the tomb of Liu Sheng. The iron blade probably belongs to a low germanium group, although it is possible that the germanium was lost on account of weathering. A minute amount of germanium is sometimes found in hematite ore. Hence, it is difficult to use germanium as a criterion in the identification of the raw material of the iron blade without a suitable iron rust serving as a standard.

Carbon. A surface sample was found by the previous chemical analysis to contain 0.35% of carbon.[29] Error in carbon determination by electron probe analysis is fairly large. Constant moving of the sample during examination may reduce the contamination of carbon caused by the interaction of the electron beam with vapour from the vacuum oil. Under the same condition, the carbon X-ray count obtained from the iron blade is only about 60% of that obtained in pure iron. It is reasonable to assume that the carbon content in the iron blade is not more than that contained in pure commercial iron.

Manganese. Using X-ray fluorescence analysis with 0.29% manganese steel as standard, the Mn content in the iron blade is estimated to be about 0.05%.

Nickel. Using X-ray fluorescence analysis with 0.29% Ni steel as standard, the average Ni content of the iron blade is about 1.8%. This is close to the value (1.76%) reported in a previous chemical analysis,[30] and to the value reported in a chemical analysis of NiO conducted by the Institute of Geology, Academia Sinica (2.5%; 1.96% Ni). Since the sample contains a copper band, the actual nickel content in the iron rust should be around 1.9–2.0%.

Chemical analysis reveals that the iron rust contains 68.74% of Fe_2O_3 and 7.84% of FeO. Converted to a copper-free sample, there should be 76.5% of Fe_2O_3 and 8.7% of FeO. Hence, the actual iron content in iron rust is about 60%. The microprobe measurement gives a figure of 45–50%. Calculated on the basis of these estimates, the nickel content should be between 3.4–4% upon reversion to metallic state.

It has been observed that, after oxidation, SnO_2 gradually disappears from the Cu_2O. Similarly, when iron-nickel alloy oxidizes to Fe_2O_3 or Fe_3O_4, the nickel oxide would also disappear from the iron oxide on weathering. The iron meteorite found at Shang-tu, Inner Mongolia, has an average nickel content of about 7.75–8.09%, while the crust after weathering contains only 3.93% of nickel.[31] The crust contains 75.29% of Fe_2O_3

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[29] Hopei Museum, "The Shang dynasty site . . . ," p. 270.

[30] *Ibid.*

[31] Oyang *et al.*, "Mineralogical studies . . ."

and 10.29% of FeO; the above nickel analysis is therefore equivalent to about 5.2% nickel in iron, i.e., about 1/3 has been lost through weathering. Cobalt decreased from 0.56%[32] to 0.24%,[33] a loss of about 40%.

In 1931, a bronze *yüeh*-axe with an iron blade and a bronze *ko*-halberd with iron head were unearthed at Hsün-hsien, Honan Province. These artifacts, dating from the end of the Shang Dynasty and the beginning of the Chou Dynasty, now in Washington, D.C., have been investigated with the help of an electron microprobe.[34] The highest nickel in the remaining iron is between 22.6–29.3%. Estimated on the basis of data given in Figure 21 in Gettens *et al.*, it contains after oxidation 13.3–16.6% nickel, which is equivalent to only about 18.3–22.6% nickel in metal, or a loss of about 30% to 33% on account of weathering. The nickel content in the iron rust is in the range of 0.5–4%, and averages between 1–2% in most areas.

Specimens taken from the iron meteorite discovered at Nan-tan County, Kwangsi, were studied with a view to determine the weathering effect on the distribution of nickel and cobalt. The results show that after weathering, the nickel content has been reduced to 2.3–10% in the high nickel area (33% Ni) and to 0.2% in the low nickel area (10% Ni). This means a loss of one half to nine tenths in this case.

The nickel content in the remaining iron rust of the iron blade unearthed at Kao-ch'eng is 2%, while its iron content is about 50%. Assuming one third of the nickel was lost through weathering, originally the iron blade should contain about 6% of nickel. Actually, iron meteorite usually transforms to Fe_3O_4 through oxidation. For instance, the iron oxides on the bronze *yüeh*-axe with an iron blade unearthed at Hsün-hsien, Honan, contain about 70–80% Fe_3O_4. But the iron rust on the bronze *yüeh*-axe unearthed at Kao-ch'eng is composed mainly of Fe_2O_3. Judging by the results of chemical analysis conducted on the Nan-tan meteorite, its nickel loss should be over one third of the original amount and the nickel content in the iron blade should be over 6%.

With electron probe microanalysis (EPMA) carried out in a direction perpendicular to the blade of the Kao-ch'eng *yüeh*-axe, the following results are obtained in the high and low nickel areas in a single scan:

	High Ni Region	Low Ni Region
Ni	2.2%	0.8%
Fe	34	9.3
O	42	16.5
Cu	21	76.1
Total	99.2%	102.7%

The areas are all located in the vicinity of the copper band, shown in Figures 22 and 23, indicating that diffusion has taken place between copper and iron in these regions. To assure that measurements of cobalt and nickel distribution would not be affected by the presence of the copper band, they were conducted only in regions containing less than 1% of copper.

Figure 32 is an Aeroview (450×) of Ni X-ray intensity (or nickel concentration) distribution in rust iron along the blade. The ridges correspond to the high nickel regions while the valleys are equivalent to the low nickel regions in the sample. The roughness

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[32] Oyang and Tong, "Chemical composition . . ."

[33] Oyang *et al.*, "Mineralogical studies . . ."

[34] R. J. Gettens, R. S. Clarke, Jr., and W. T. Chase, *Two Early Chinese Bronze Weapons with Meteoritic Iron Blades* (Washington, D.C., 1971) Freer Gallery of Art, Occasional Papers, vol. 4, no. 1.

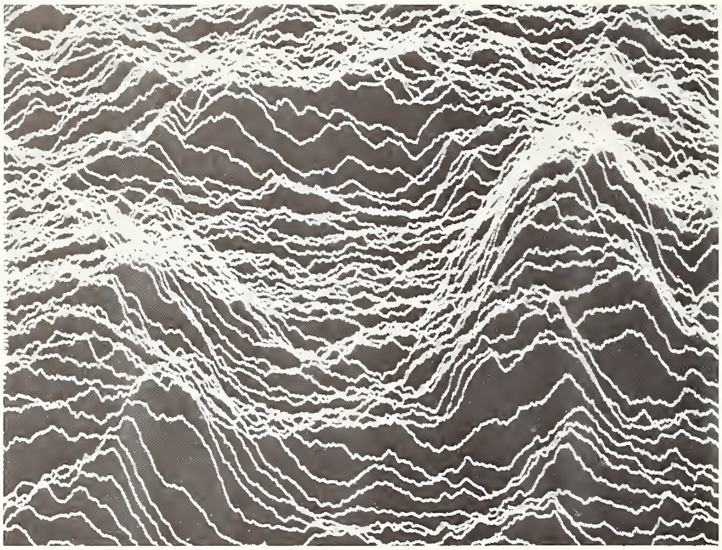

FIG. 32.—Aeroview image of nickel distribution in the Kao-ch'eng *yüeh*-axe. 450 × .

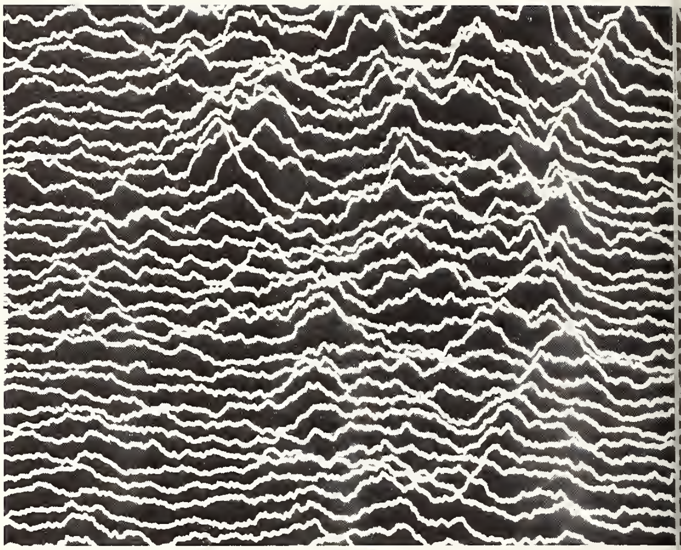

FIG. 33.—Aeroview image of nickel distribution in a region different from Figure 32 in the Kao-ch'eng *yüeh*-axe. 500 × .

of the curves is due to X-ray fluctuations and the uneven loss of nickel during weathering. Apparently, its nickel distribution is similar to that of the Dzungarian (Armanty) iron meteorite (fig. 17). The high nickel regions have an average length of over 100–170 μm and a width of about 30–60 μm. During forging and weathering, the nickel would diffuse from the high concentration area toward the lower area. Hence the original high nickel zone should have a higher nickel content but a narrower width.

Using pure Ni as a standard and the iron rust of the iron sword unearthed from the Tomb of Liu Sheng at Man-ch'eng for X-ray background corrections, the highest and lowest nickel concentrations in the region covered by Figure 32 have been measured. After corrections, the highest figure for nickel content is 4.2% and the lowest is 1.06%, which correspond to 8.4% and 2.1% of nickel in iron (not counting weathering loss), or 12% and 3% in iron (including the estimated minimum weathering loss) respectively.

Figure 33 is an Aeroview of another region of the same sample as shown in Figure 32. It has the same M-shape in the Aeroview of nickel distribution but is narrower in width.

Figure 34 shows the nickel distribution of another area using an X–Y recorder. The portion on the right-hand side is a continuation of the one on the left. Each curve represents the nickel distribution along the sample perpendicular to the Aeroview traces (fig. 33). The whole width is 0.24 mm. The distance between the two neighboring curves is 16.7 μm, while the length covered is 0.2 mm along the blade. The lamellar distribution of nickel is also very distinct here, sometimes attaining a length of over 0.2 mm and a width of about 20–40 μm. The extent of concentration fluctuation can be estimated from the height of the vertical index given in the figure. The highest nickel content in this figure is 2.2%, while the greatest difference in the nickel contents of neighboring areas is around 1.2–1.4%.

Cobalt. The same method was used to determine the content and distribution of cobalt. Taking a steel sample with 0.145% of cobalt as a standard, X-ray fluorescence study of the iron blade has yielded an average cobalt content of 0.21%, which approximates the figure of 0.24% CoO (or 0.19% Co) obtained through chemical analysis. Figure 35 shows the cobalt distribution of the same

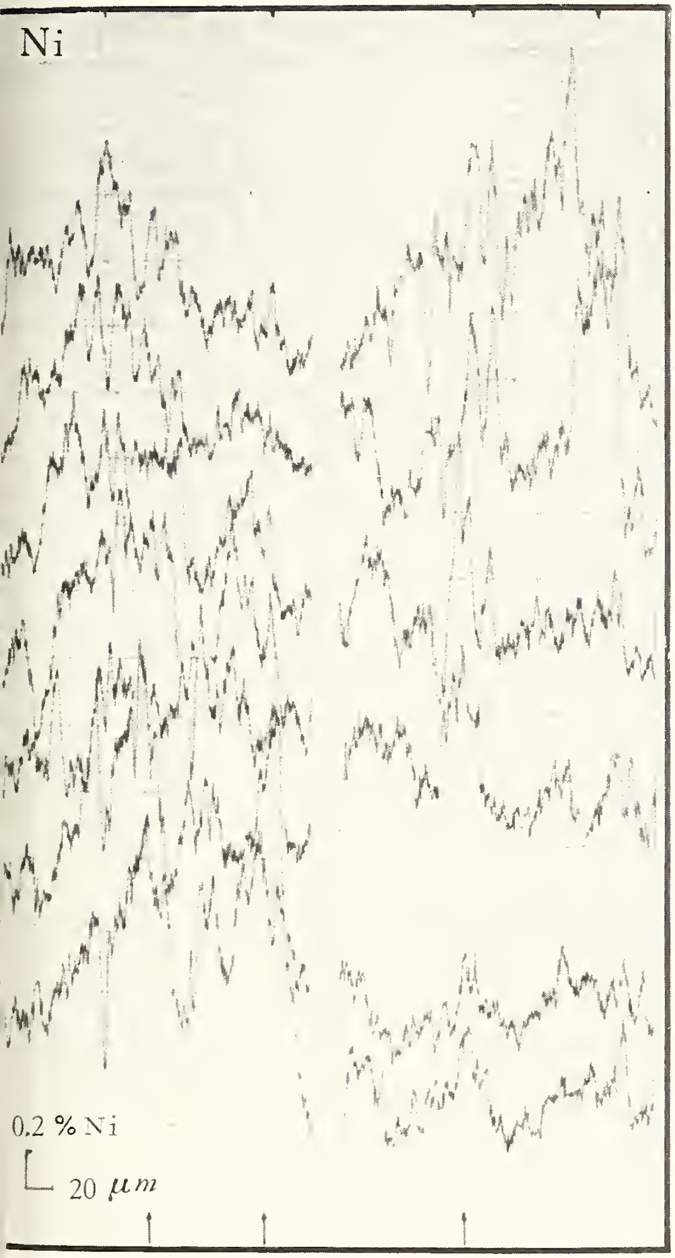

Fig. 34.—Nickel distribution in the iron blade. 500 ×.

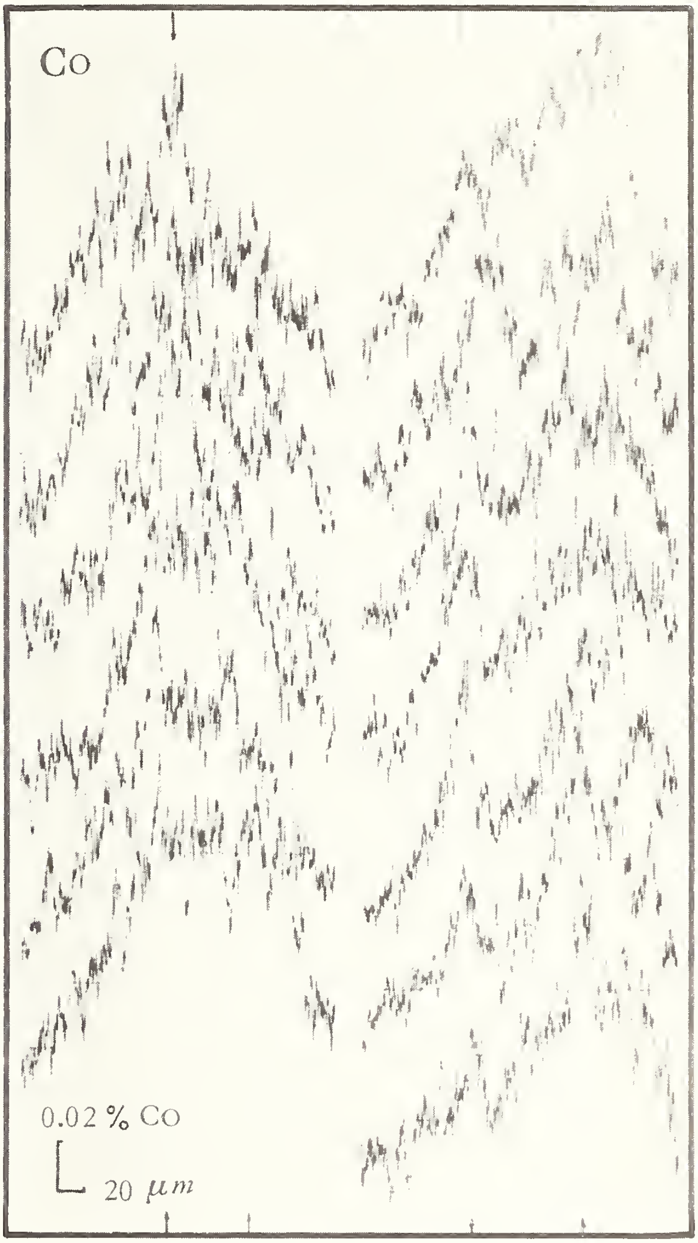

Fig. 35.—Cobalt distribution in the iron blade. 500 ×.

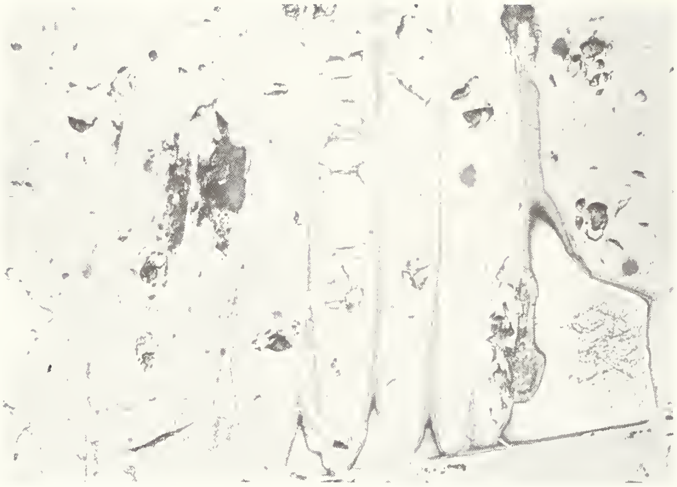

Fig. 36.—Microstructure of the partially oxidized Nan-tan meteorite. 200 × .

Fig. 37.—Microstructure of the partially oxidized Nan-tan meteorite. 253 × .

area as shown in Figure 34. Its highest Co content is 0.16% while the lowest is close to zero. Due to the use of a LiF analyzing crystal of high resolution, the X-ray count drops radically as we move from the center, thereby causing a curvature in the individual curves. It can be seen, however, that the cobalt distribution is also of the type similar to that found in the nickel distribution.

In the case of iron meteorites, cobalt segregates in α while the γ is enriched with nickel as shown in Figure 11. Probably because of the different loss rates of nickel and cobalt oxides during weathering as a result of differences in the nickel and cobalt contents, such correspondence between nickel and cobalt is not conspicuous in the iron blade.

For the purpose of checking whether the nickel and cobalt distribution observed in the iron blade is related to its meteoritic origin, and acquiring a better understanding of the loss of nickel and cobalt during weathering, the Nan-tan iron meteorite and its weathered crust were investigated. The Nan-tan iron meteorites, probably fragments of a meteorite known to have fallen in A.D. 1516, were first found in 1958. These are octahedrites with a nickel content of 6.98–7.26%. In the present study, some partially weathered samples and completely weathered samples (crusts) were used. The metal parts of the former have an average nickel content of 5.9%, while the oxides have a nickel content of 1.4% (or 2% Ni in iron).

Figure 36 represents the microstructure of the partially weathered sample, in which remnants of a Widmanstätten structure are still visible. The light fragments are metallic α while the intervening phase, located between the partially oxidized plates, has been weathered to gray oxide with traces of dark gray high-nickel regions. Figure 37 shows the structure of another region. The middle band represents the original γ-phase; some small γ-phase fragments remain in the lower left while the middle oxidized region resembles the oxide of α, though still retaining high nickel traces in a darker shade. Their nickel and cobalt contents are as follows (those shown in a parentheses are taken from another area):

	Ni%	Co%
γ-phase		
remaining metal	33	0.24
	(48)	(0.45)
light gray oxides	3.4–10	0.2–0.36
dark gray oxides	2.3–3.5	0.05–0.31
	(6–16)	(0.29–0.43)
α-phase		
remaining metal	10	0.79
light gray oxides	0.20	0.35
	(0.3–0.7)	(0.28–0.46)
dark gray oxides	~0	0.36

The above results show that long weathering of an iron meteorite has caused the high nickel in γ-phase to drop from 33–48% to 2.3–16% (or 3.3–23% Ni in iron), which means a loss of 50–90%. The nickel in the low nickel region (original α-phase) drops from 6–10% to 0.2–0.7% (0.3–1.0% Ni in iron). The cobalt content of 0.24–0.79% in the original metal has dropped to 0.05–0.46% (or 0.09–0.63% in metal) after weathering, which means a loss of 20–60%. Figure 38 is a micrograph of the crust sample which has been completely weathered. Figure 39 is an Aeroview of nickel distribution in the same area, and Figure 40 shows a conventional electron probe microanalysis (EPMA) trace on nickel. The highest nickel is 11% and the lowest is 0.7–1.5%. Cobalt ranges between 0.01–0.21%, but shows no correspondence with the nickel distribution. It can be seen from these results that the nickel distribution in a totally weathered meteorite is similar to that found in the bronze *yüeh*-axe with iron blade unearthed at Kao-ch'eng. In addition, the weathered Nan-tan meteorite has a residual nickel content close to that found in the iron blade. Hence, it is quite possible that the highest nickel in the iron blade before weathering was much higher than the conservative estimation given above, and might actually be over 30%. Such a lamellar nickel distribution can only be obtained with a cooling rate of 1–10°C/m.y. between 700°C to 400°C. We can, therefore, conclude that the iron blade on the Kao-ch'eng bronze axe was made of iron meteorite.

Inclusions near the Fracture of the Iron Blade

It is mentioned in the original report that calcium-bearing and silicon-bearing particles have been observed near the fracture of the iron blade. The fact that their shape and main constituents are similar to those found in the inclusions in steel has led to the suggestion that the blade was probably made from man-made iron. To determine the nature of these included particles, the specimen previously studied was reexamined with optical and scanning electron microscopes. Qualitative analysis of the inclusions was carried out with a lithium-drifted silicon detector mounted on the SEM, which identifies the chemical elements present and measures the intensities of X-rays generated by the impact of electrons upon the specimen surface. The X-ray intensity from a particular element gives a measure of its content at that particular point. The detector is incapable of detecting elements with atomic number smaller than oxygen, and fails accordingly to distinguish oxide, hydroxide and carbonate.

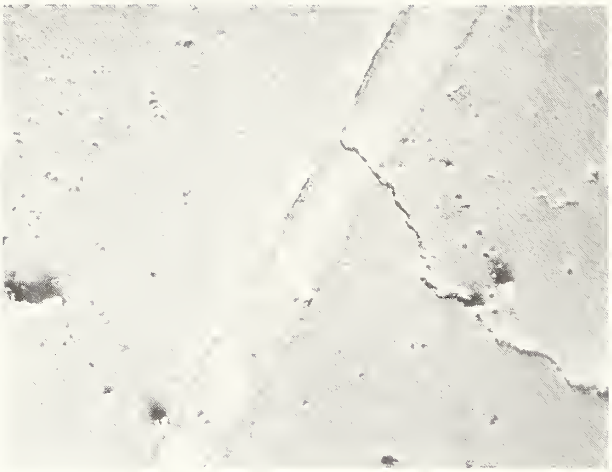

FIG. 38.—Secondary electron image of the oxide scale of the Nan-tan meteorite.

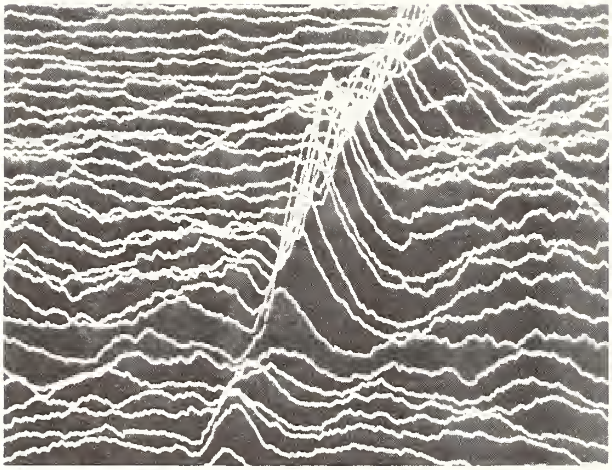

FIG. 39.—Aeroview of the nickel distribution in the region shown in Figure 38.

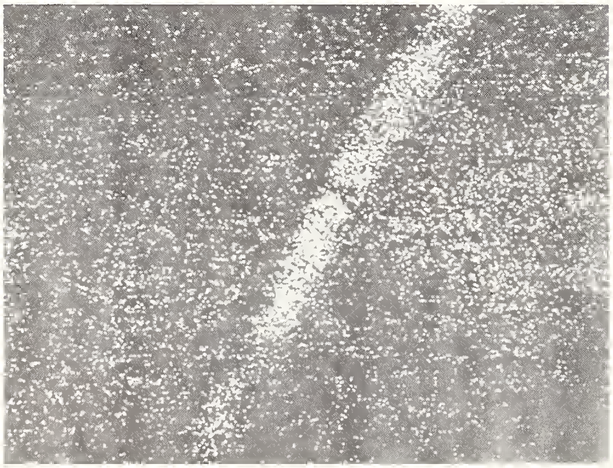

FIG. 40.—Nickel distribution in the sample in Figure 38.

Because of the fine electron beam used in the SEM, the chemical composition at various locations of the same inclusion particle can be analyzed. The following examinations were generally made at magnifications between 1000 × − 2000 × ; some were done at 5000 × .

The results show that samples obtained from the surface differ from those obtained from inside the iron blade and contain particles of all shapes and sizes. In spite of a certain resemblance to the inclusions in steel, they are marked by the following characteristics:

(1) They often appear in groups as shown in Figure 41. The light particles 1,2 and 3 are mainly iron oxide, the gray particles 4 and 8 are quartz, and 5,6 and 7 are oxides of silicon and aluminum with some calcium; 7 also contains potassium. All these particles contain some chlorine, which is absent from the iron rust matrix. Some of the particles are rather large in size and parallel to the sample surface, sometimes with regular shapes, particularly the quartz particles.

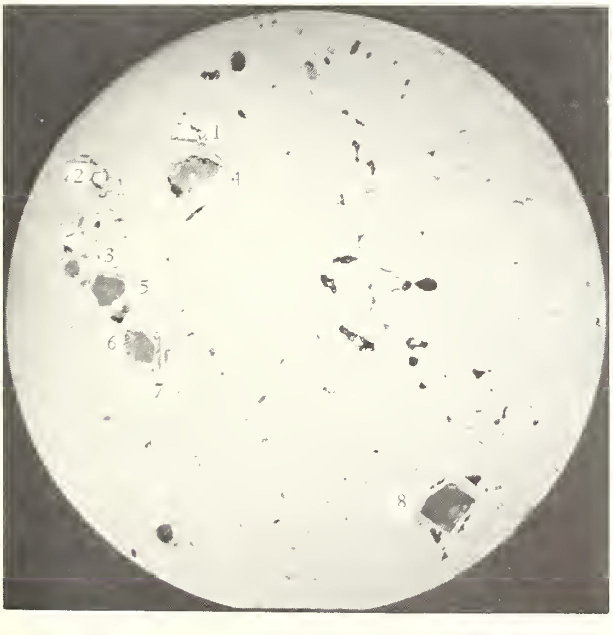

Fig. 41.—Microstructure of specimen 1 in Figure 1 from the contaminated surface of the *yüeh*-axe. Optical micrograph. Unetched. 200 × .

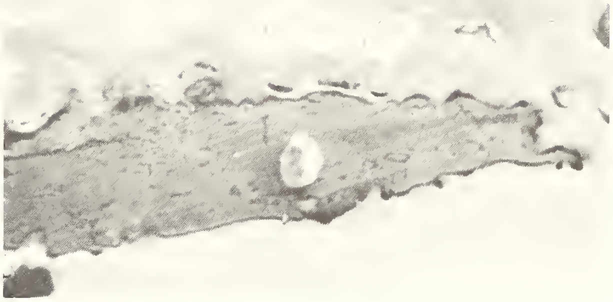

Fig. 42.—SEM image of the inclusions in specimen 1a in Figure 2 taken near the fracture of the iron blade. Unetched. 590 × .

(2) The compositions are rather complicated. The particles shown in Figure 41 contain chlorine which is never found in man-made iron. On the surface which contained the silicate inclusions, the particles contain not only the silicon and iron previously reported by HSR, but also significant amounts of Mg, Al, Ca, and some Cl, S and K. One of these particles is shown in Figure 42. On the surface where calcium-bearing stringers were originally observed, calcium-bearing matter is found along with Mg, Si, S and Fe. After polishing with chromium oxide (Cr_2O_3),[35] some of the materials start to peel off, exposing corrosive pits as shown in Figure 43. The lower part of the pit shown in the figure still contains some $Ca(OH)_2$ or $CaCO_3$, which would disappear upon further

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[35] The specimen had been shown by X-ray energy spectroscopy to be free from chromium before polishing. It was then polished with Cr_2O_3 with a view to avoiding any possible misleading results or conclusions due to contamination by the polishing agent.

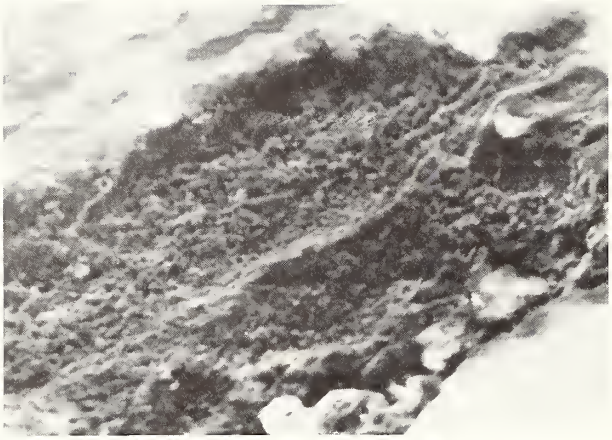

FIG. 43.—SEM image of the specimen 1b in Figure 2 taken near the fracture of the iron blade, showing calcium deposit in a corrosion pit on the surface. 150 × .

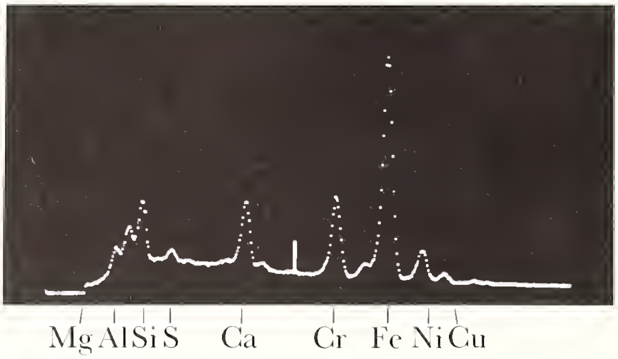

FIG. 44.—X-ray energy spectra of an inclusion in specimen 1 in Figure 2 taken near the fracture.

polishing. This shows that the calcium-bearing materials were deposited in the pits. It also suggests that the deposition took place after the corrosion pits had been formed.

In order to preserve the pitting surfaces, the third surface (fig. 2, 1c) was prepared by repeated polishing. A large number of inclusions are observed, and Figure 44 and 45 represent the X-ray spectra obtained from two of these particles. One of them contains mainly Fe_2O_3, and some Ca, Si and Al as well as a small amount of Mg, S, and Cu; the other mainly Si with some Al, Mg and Ca.

(3) Inhomogeneities in composition. When the sample was being repeatedly polished, new particles appeared. But some large thick particles could still be examined layer by layer. The inclusion shown in Figure 46 exhibited the composition given in Figure 45 and consisted mainly of silicon. As the specimen was further polished, the inner layers exhibit 2–3 times more aluminum. Meanwhile, K, Na and Ti appear and the amount of Mg decreases.

Similarly, the composition of a particle in the same layer often varies from point to point. In Figure 47 curves 1–14 were obtained from the inclusions of Figure 48.

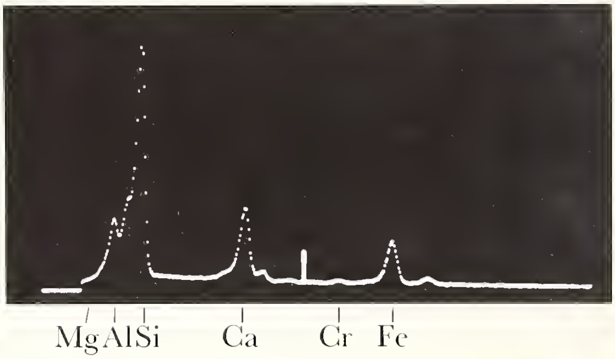

FIG. 45.—Energy spectrum of the inclusion in Figure 46.

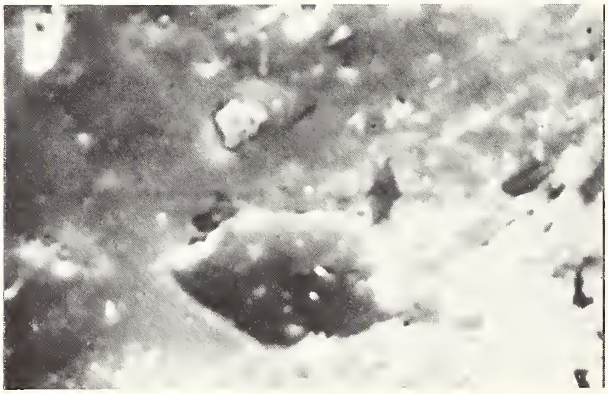

FIG. 46.—SEM image of inclusions of the iron blade near the fracture. Specimen 1c in Figure 2. 430 × .

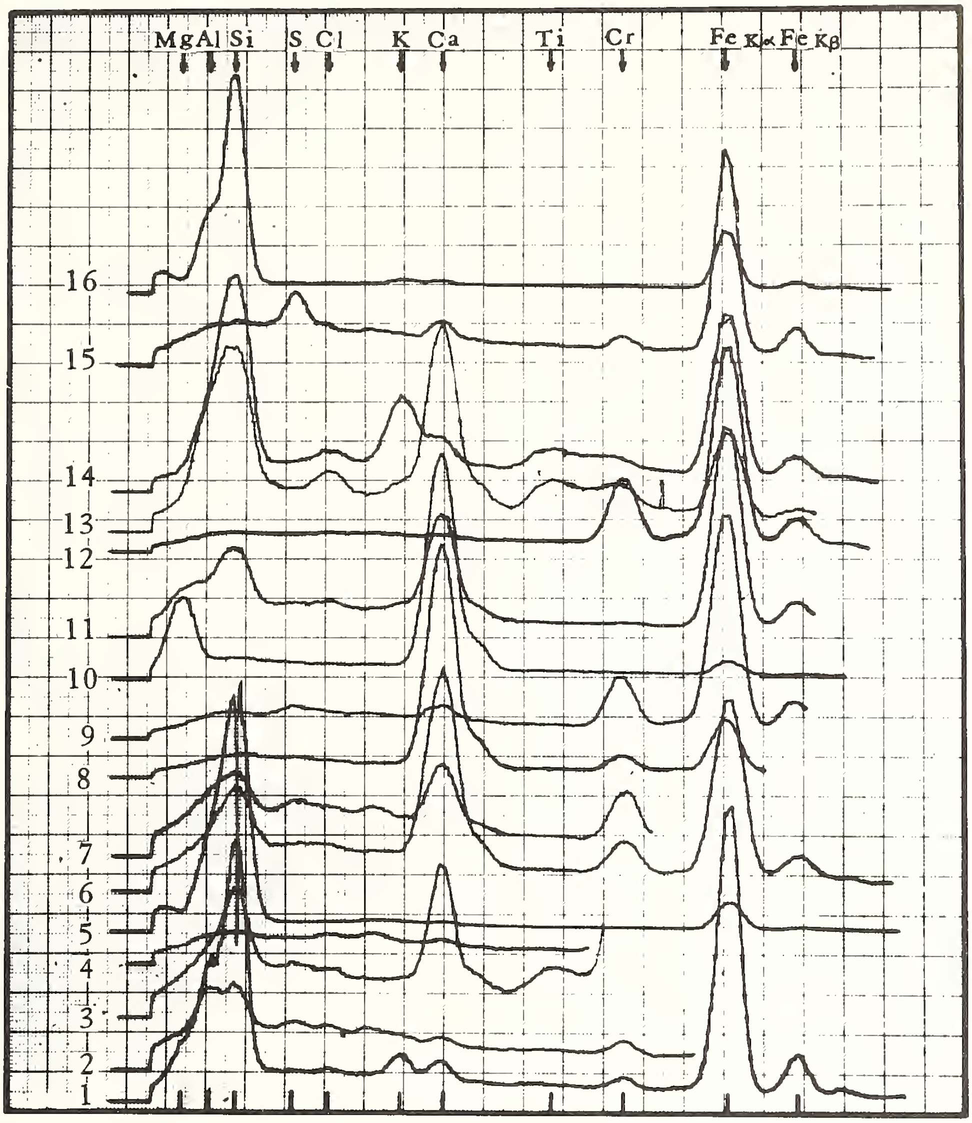

FIG. 47.—X-ray energy spectra of inclusions in Figure 48. Note: X–Y recordings similar to Figure 44 and Figure 45. Each curve has been displaced vertically to avoid overlapping. The iron peaks of curves 2, 3, 4 and 7 have been omitted for the same purpose.

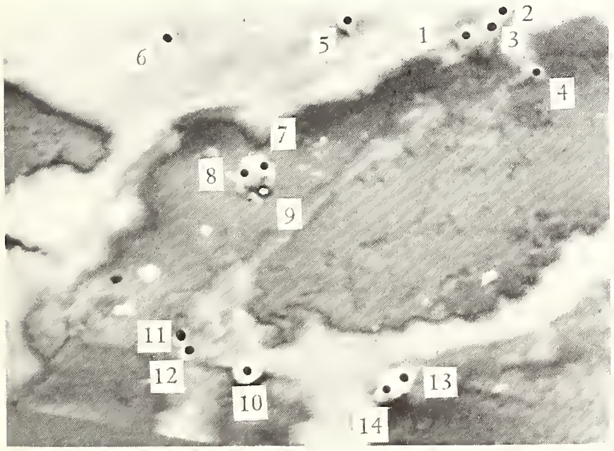

FIG. 48.—Same as Figure 46, 288×. The numbers correspond to the curves in Figure 47.

Curves 1,2,3; 7,8,9; and 13,14 were obtained from various points of three separate inclusions. Curves 15 and 16 were obtained from two other included particles. All these curves show not only that different particles have varying compositions, but also that in one particle the composition may vary from point to point. For instance, curve 13 shows that the inclusion contains Fe, Ca and a small amount of Cl, Ti, while curve 14 contains mainly Si and a larger quantity of K as compared to curve 13.

These results indicate that the chemical compositions of the so called inclusions near the fracture of the iron blade vary extensively. These particles contain some impurities that have never been found in ancient man-made iron, such as Cl, Na and Cu, and infrequently K and Ti, etc. Their compositions differ from those of inclusions in either ancient or modern man-made iron. Analyses of inclusions in ancient man-made iron[36] show that all the inclusions in the same artifact are of the same kind and their compositions are basically the same (fig. 4).[37]

In conclusion, the so-called inclusions found in the Kao-ch'eng iron blade differ from inclusions of man-made iron. These included particles were formed by precipitation as a result of long burial and reaction with underground water containing dissolved minerals. This fact is further proved by the structure shown in Figure 49. The latter is obtained from position (la) in Figure 2 with scanning electron microscope after polishing. The light area is copper oxide while the dark one consists of iron oxide. Clearly, they are corrosion products of the *yüeh*-axe deposited in alternate layers.

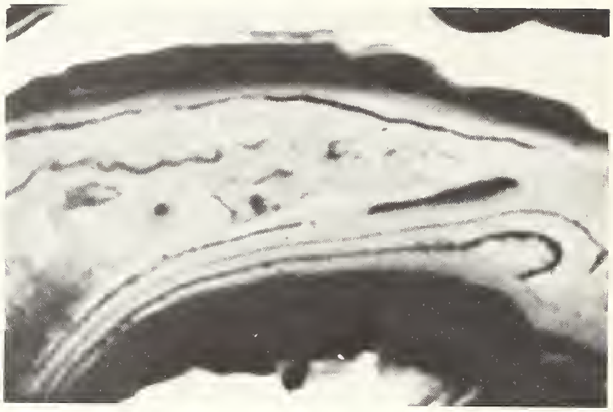

FIG. 49.—Laminated copper and iron deposits near the fracture surface of the iron blade. Specimen 1a in Figure 2. 400 × .

CONCLUSIONS

Origin of the Iron Blade

The Kao-ch'eng iron blade does not contain the same inclusions as those found in man-made iron. The original specimen is believed to have contained more than 6% nickel and over 0.4% of cobalt. Even after metal-working and long weathering, the rusted iron blade still preserves the lamellar distribution of nickel and cobalt. The nickel content of the high nickel region before weathering was above 12% or even as high as over 30%. This lamellar distribution of nickel could only occur in an iron meteorite as a consequence of very slow cooling. Based on these results and by comparison with iron meteorites and their weathering crusts, a definite conclusion can be drawn that the Kao-ch'eng *yüeh*-axe iron blade was not made of smelted iron, but rather of an iron meteorite.

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[36] Li Chung, "The development of iron and steel . . ."

[37] Figure 4 shows the spectra from different parts of the inclusion shown in a directly-reduced iron datable to ca. 500 B.C. The smooth curves, 3 and 5, indicate that few impurities are present in the wustite (FeO) particles (light shade in fig. 3); the peaks on the other spectra indicate the impurities contained in the fayalite-wustite eutectics (dark interstices in the inclusion). Iron peaks with much greater heights on the right are not shown in these spectra.

The Included Particles in the Surface Layer of the Blade

There are silicon-bearing and calcium-bearing inclusions with complicated chemical compositions near the surface of the iron blade. These are foreign materials deposited in the blade after weathering rather than original inclusions in the iron blade.

Copper Layer in the Iron Blade

The fact that the iron blade was made from an iron meteorite explains the formation of the copper bands shown in Figure 22. These banded structures are composed of alternate copper and iron layers. The copper layer ranges in thickness from 10 to 35 μm, while the iron layer ranges from 10 to 55 μm. This layer contains nickel, but the copper layer does not. These observations indicate that the banded structures differ from the deposited layer structures as shown in Figure 49, and could only be formed if the blade was made from a material containing microconstituents of vastly different deformabilities. If such a material were worked, the low nickel α-phase (kamacite) would extend more easily than the high-nickel γ-phase (taenite), producing ragged edges and making gaps. When the bronze was being cast onto the blade, it could have flowed into these gaps and formed copper layers, sandwiched between nickel-bearing iron layers, as is observed in the specimen. Such a banded structure would not be seen in pure iron, low carbon or low alloy steel because of uniform deformability during the working process. While an iron meteorite can be cold-worked, cracks due to work-hardening will probably form in the process. Some flaws 5–10μm in width filled with copper occur in the iron blade near the the copper band. Bronze has good castability and wettability, and would flow into the cracks. These cracks were formed during the cold-working process and were subsequently filled with bronze during casting.

The Kao-ch'eng *yüeh*-axe was thus made by casting bronze around the tang of the blade wrought from meteoritic iron.[38] It is remarkable that by the middle of the Shang Dynasty people were already capable of forging an iron-nickel alloy to a thickness of less than two millimeters. Indeed, the *yüeh*-axe is a fine example of the attainments that a slave artisan could accomplish with tools so primitive.

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[38] A similar bronze *yüeh*-axe of the same period (middle Shang), 84 mm long and 50 mm wide, with nickel-bearing iron blade, probably meteoritic in origin, has been unearthed recently near Peking. See "Excavation of a Shang Dynasty Tomb at Pingku County, Peking," *Wen Wu*, (*Cultural Relics*), 1977, no. 11, p. 1.

THE TECHNIQUES OF THE JAPANESE TSUBA-MAKER

By ELAINE I. SAVAGE*
and CYRIL STANLEY SMITH**

Introduction

The Japanese have been more sensitive than most peoples to the inner nature of materials and this underlies the distinctive character of their decorative art. The materials of the tea ceremony—ceramics, metal, stone, plaster, bamboo, lacquer and wood—all have subtle surface qualities that interact with and reinforce the overall aesthetic requirements of the form. These qualities arise directly from structural nuances on both visible and microscopic levels and are affected by the physical and chemical behavior of the materials during their preparation. Regions of differing atomic or crystalline structure are produced in response to microscopic variations of composition, deformation or temperature, and in the best work the resulting geometry harmoniously relates the smallest features to the largest ones—the molecular or crystalline forms at one end and conscious positioning of matter by the craftsman at the other. These physical effects become particularly exciting when viewed in association with the connoisseur's customary enjoyment of the abstract beauty, craftsmanship and cultural overtones embodied in the work.[1]

There is an extensive Japanese literature on native metalworking techniques.[2] In Western languages the first account was by Raphael Pumpelly in 1866,[3] but even today there is little beyond what is found in the general handbooks for metal craftsmen by Wilson,[4] and by Untracht,[5] and the appropriate sections of the surveys of Japanese industries made at the end of the nineteenth century by Rein[6] and Brinkley.[7] Near the turn of the century two eminent British metallurgists, Roberts-Austen[8] and Gowland[9] presented excellent technical discussions of

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[1] For a discussion of decorative effects residing in the properties of matter see C. S. Smith, "Metallurgical Footnotes to the History of Art," *Proc. American Philosophical Society*, vol. 116 (1972), pp. 47–135; C.S. Smith, "Reflections on Technology and the Decorative arts," in I. A. Quimby and P. A. Earl, eds., *Technological Innovations and the Decorative Arts*, Winterthur Conference, 1973 (Charlottesville, Virginia, 1974), pp. 1–62; C. S. Smith, "A metallographic examination of some Japanese sword blades," *Documenti e contributi per la storia della metallurgia*, no. 2 (1957), pp. 42–68.

[2] A good recent book on the technical terminology relating to sword furniture is H. Wakayama, *Tō-sogu kodogu koza* . . . (Japanese Sword Furniture: Terminology . . .) (Tokyo 1974).

[3] R. Pumpelly, "Notes on Japanese Alloys," *American Journal of Science*, vol. 42 (1866), pp. 43–45.

[4] H. Wilson, *Silverwork and Jewellery* (London, 1951, 2nd ed.) contains a section on Japanese techniques written by Unno Bisei, pp. 321–367.

[5] O. Untracht, *Metal Techniques for Craftsmen*, (Garden City, N.Y.: Doubleday, 1968).

[6] J. J. Rein, *The Industries of Japan* (New York, 1889).

[7] F. Brinkley, *Japan, its History, Art and Literature*, 8 vols. (London, 1903–4); Metallurgy and metalworking are discussed in Vol. III.

[8] W. C. Roberts-Austen, "Cantor Lectures on Alloys: Colours of Metals and Alloys Considered in Relation to their Application to Art," *Journal of the Society of Arts*, vol. 36 (1888) pp. 1137–1146; and "Application of alloys in metalwork," *Journal of the Society of Arts*, vol. 41 (1893), pp. 1022–43.

[9] W. Gowland, "Metals and Metalworking in Old Japan," *Transactions of the Japan Society of London*, vol. 13 (1915), pp. 20–100.

Japanese metalwork and included many chemical analyses, although they did not of course at that time perform metallographic studies. There are also many exhibition catalogues, sales catalogues and other publications aimed at the collector and connoisseur that are profusely illustrated with excellent photographs of different classes of work and contain useful summaries of the techniques, but these are rarely based on direct practical experience with the materials and the tools.[10] The fine recent catalogue of the Japan House exhibition of the Walter A. Compton collection of swords and tsuba[11] contains a good account of techniques and terminology written by Morihiro Ogawa and should be referred to for a glossary of terms.

The processing of a metal changes its microstructure, and in the microstructural details can be found a record of much of an object's technical history. Unfortunately, a complete study requires the removal of a section, and such destruction is intolerable with any object of beauty or value. However, damaged objects are sometimes available. There are in the Bigelow collection at the Museum of Fine Arts, Boston, a number of tsuba, the integrity of which had been ruined in the 1880's by a thief, in an attempt to remove the *shakudō* and gold inlay.[12] From these tsuba, it was possible to remove sections large enough for metallographic examination. Details of workmanship can also be inferred by close examination of the surface under the microscope, and many tsuba were studied in this non-destructive way.

CHEMICAL ANALYSIS

The principal tsuba examined are described in Table 1 and are shown in Figures 1–5. Table 2 gives the results of chemical and spectrographic analyses of some of the component materials. The iron and the copper alloys of which the tsuba are made have been repeatedly mentioned in the literature and the analytical results present no surprises. (*Shibuichi* and *shakudō* are copper alloys popular in Japan but unique to that country, containing nominally about one quarter silver or a few percent of gold, respectively.) Both of the iron tsuba, Numbers 1 and 2, have only traces of impurities; there is no evidence of intentional alloying. The many minor constituents in the copper alloys are probably unintentional impurities, although the amounts of arsenic and iron present in some samples are high enough to have an effect on patination and may indicate a deliberate selection of the raw materials. The presence of over 1% silver in the *shakudō* inlay in the guard by Goto Ichijo should be noted.

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[10] H. C. Gunsaulus, *Japanese Sword Mounts in the Collection of the Field Museum* (Chicago: Field Museum Publication No. 216, 1923); J. D. Hamilton, *The Peabody Museum Collection of Japanese Sword Guards* (Salem Mass., 1975); S. Hara, *Die Meister der Japanischen Schwertzieraten* (Hamburg; 1931); J. Homma, ed., *Masterpieces of Japanese Swordguards* (Tokyo: Society for Preservation of Japanese Art Swords, 1952); H. L. Joly, *Japanese Sword-mounts: Descriptive Catalogue of the Collection of J. C. Hawkshaw* (London, 1910); H. L. Joly, *Catalogue of the G. H. Naunton Collection of Japanese Sword Furniture* (London, 1912); H. L. Joly, *Sword Fittings in the W. L. Behrens Collection* (London, 1912; reprint, New York, 1966); H. L. Joly, *Japanese Sword Guards in the Collection of Sir Arthur Church* (1914; reprint, Tokyo, 1969) (The collection is now at the Ashmolean Museum, Oxford); S. H. Moran, "Some Notes on Japanese Sword Accessories," *Oriental Art*, N.S. vol. 9 (1973) pp. 50–59, 180–191; B. W. Robinson, *The Arts of the Japanese Sword* (London: Faber and Faber, 1970; 2nd ed.); M. Sasano, *Early Japanese Sword-guards—Sukashi tsuba*, (Tokyo and San Francisco, 1972); G. C. Stone, *A Glossary of the Construction, Decoration, and Use of Arms and Armour in All Countries in All Times*, (London, 1934; reprint, New York, 1961); J. Van Daalen, *Catalogue . . . of the Collection of Japanese Sword Furniture of the Late General J. C. Pabst* (The Hague, 1956). The last is a useful listing of Japanese metalworking techniques and their terminology.

[11] W. A. Compton, J. Homma, K. Satō and M. Ogawa, *Nippon-tō; the Art Swords of Japan* (New York: Japan Society, Inc, 1976).

[12] With the tsuba is the following note: "Tsuba for study purposes: these 19 tsuba were stolen from Dr. William Sturgis Bigelow's house in Tokyo. When they were reclaimed by the police, the thieves had removed the gold inlay. They are to be kept unaccessioned for study purposes, to show the depth of inlay, and signatures; for analysis of metals; etc."

Table 1

Tsuba used for Metallographic Study
(All are in the study collection of the
Museum of Fine Arts, Boston)

No. 1 (Fig. 1)	Iron. Soten school, probably late eighteenth century. 8.0 cm diameter, 4.2 mm thickness at *seppa-dai*. (M.I.T. No. 403.)
No. 2 (Fig. 2)	Iron. Signed Taira Yoshihiro, "made of *nambantetsu*". 8.0 cm diameter, 4.6 mm thickness. (M.I.T. No. 404.)
No. 3 (Fig. 3)	Brass. Signed Shiunsai Hirochika, with seal. Mid-nineteenth century. 8.5 cm diameter, 4.0 mm thickness. (M.I.T. No. 406.)
No. 4 (Fig. 4)	*Shibuichi*. Signed Goto Hokkyo Ichijo. Mid-nineteenth century. 7.0 cm diameter, 5.1 mm thickness at rim. (M.I.T. No. 407.)
No. 5 (Fig. 5)	Brass. Signed Hamano Noriyuki. Nineteenth century. 8.5 cm diameter, 4.0 mm thickness. (M.I.T. No. 428.)

HARDNESS

The hardness measurements, listed also in Table 2, are not particularly revealing. The copper inlay is the softest, the iron the hardest. The considerable variations in hardness in different parts of the same metal are due mainly to differing amounts of cold deformation, although variations in grain size and in the iron, carbon and slag content have considerable influence also. None of the iron shows evidence of intentional carburization or of hardening by heat treatment.

MICROSTRUCTURE OF THE IRON TSUBA

The iron tsuba, when examined in cross section under the microscope, showed some interesting features.[13] The Yoshihiro tsuba, Number 2, bore an inscription stating that it was made of *nambantetsu*, "iron of the southern barbarians," that is, iron imported by the Portuguese merchants. The microstructure (figs. 6 and 7) shows unmistakably that this sample is nothing but wrought iron of rather inferior quality, heterogeneous in structure, containing many slag inclusions, and with a carbon content that varies greatly from place to place. (The carbon content is inferred from the amount of the dark-etching, finely duplex microconstituent, known to metallographers as pearlite, which is visible within the grains in fig. 6).

The grain size varies throughout the sample but is always small, indicating that forging was finished at a low temperature, while the

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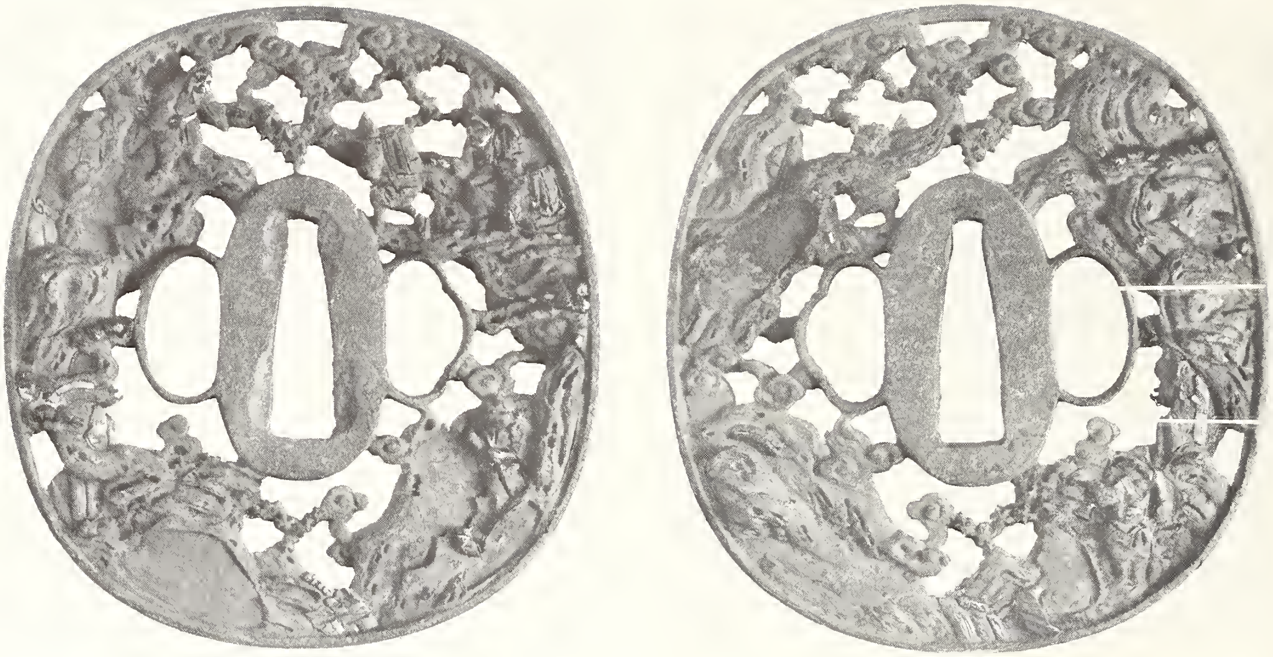
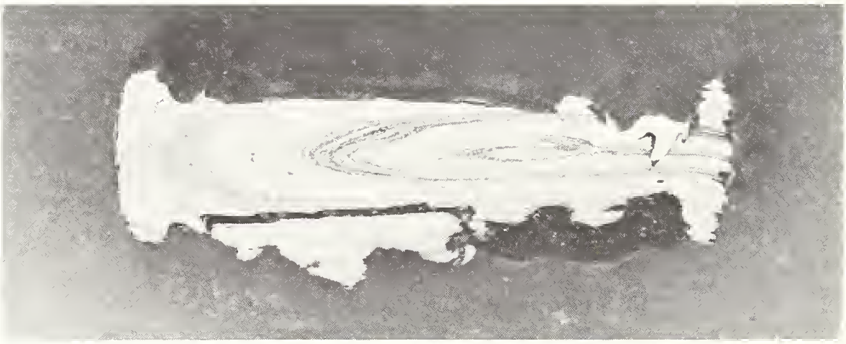
[13] In the accompanying photomicrographs, unless otherwise indicated, all iron microsamples were etched with nital (2% nitric acid in alcohol).

1a. 1b.



1c.



1d.

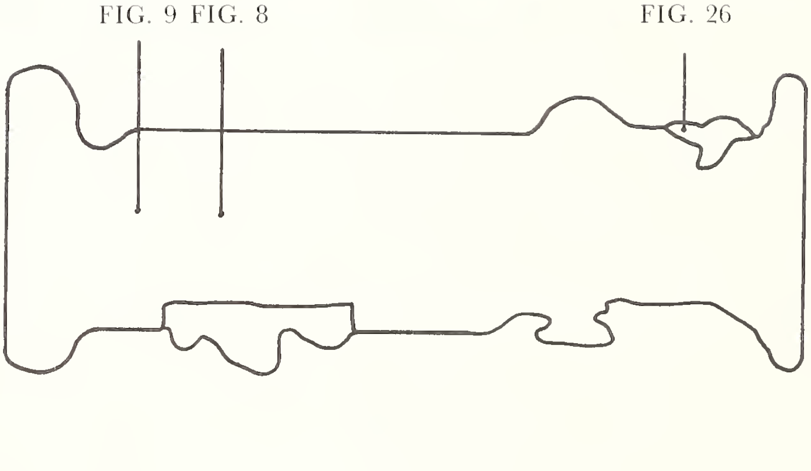
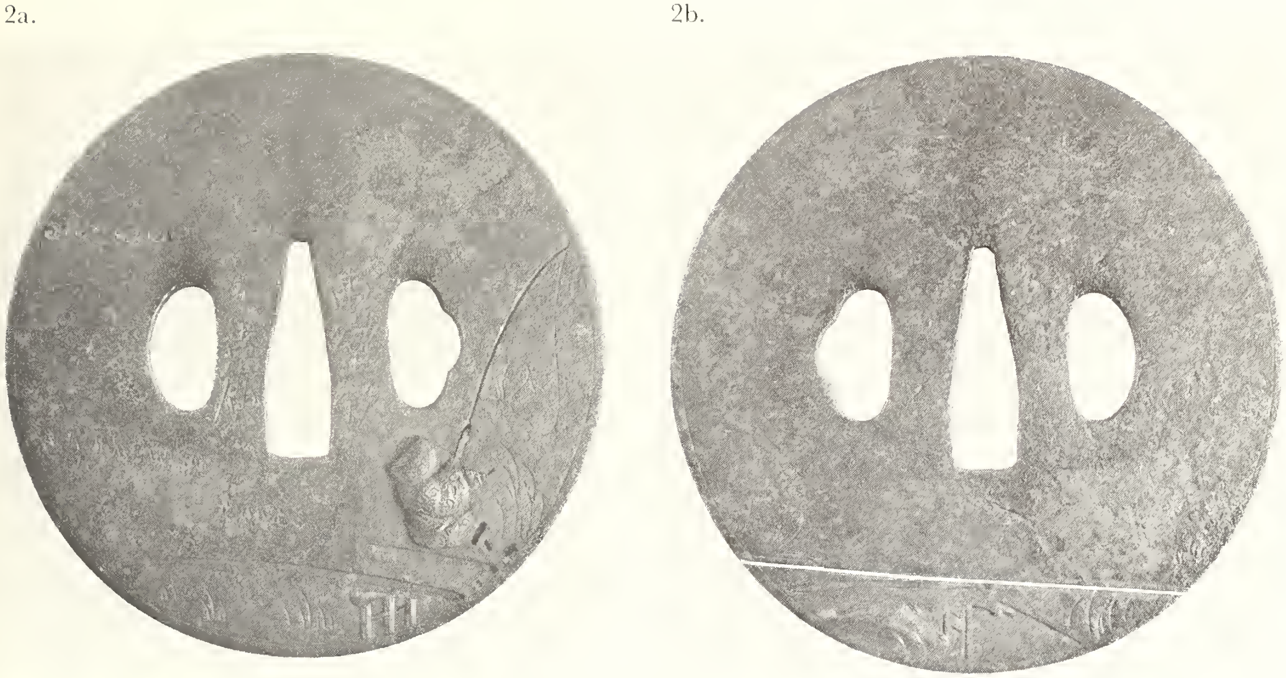
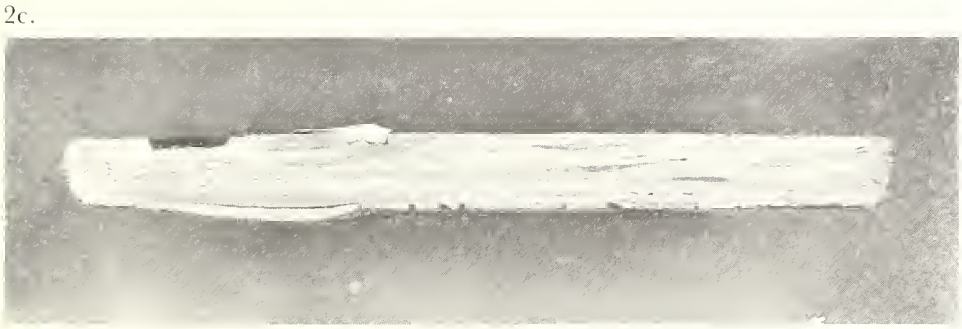


Fig. 1.—Tsuba no. 1. Iron, damaged. Soten school. a. Obverse, natural size. b. Reverse, natural size, showing location of section removed for analysis. c. Cross section, etched, X4. d. Diagram showing location of photomicrographs.





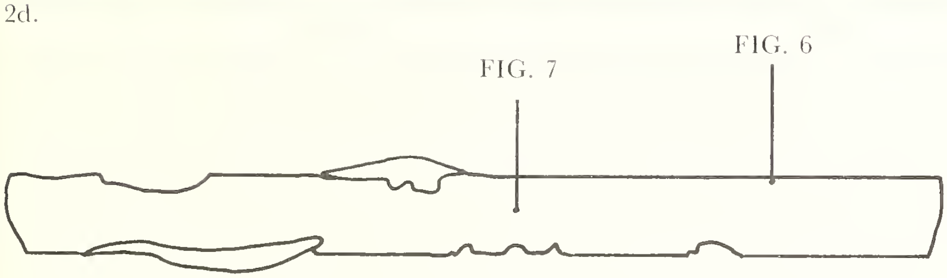


Fig. 2.—Tsuba no. 2. Iron, damaged. Inscribed "*Nambantetsu*, made by Taira Yoshihiro." a. Obverse, natural size. b. Reverse, natural size, showing location of section removed for analysis. c. Cross section, etched, × 3.3. d. Diagram showing location of photomicrographs.

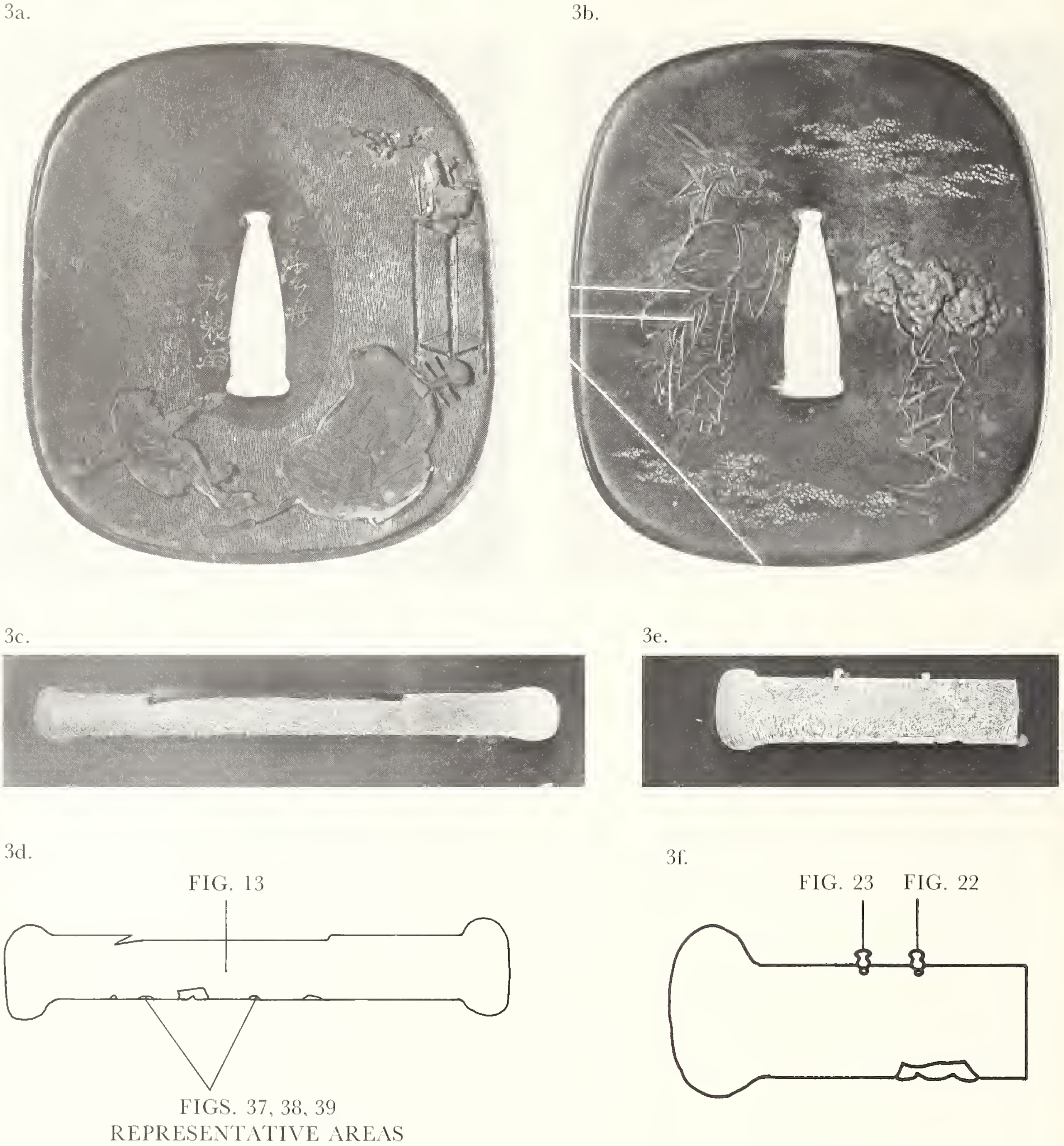
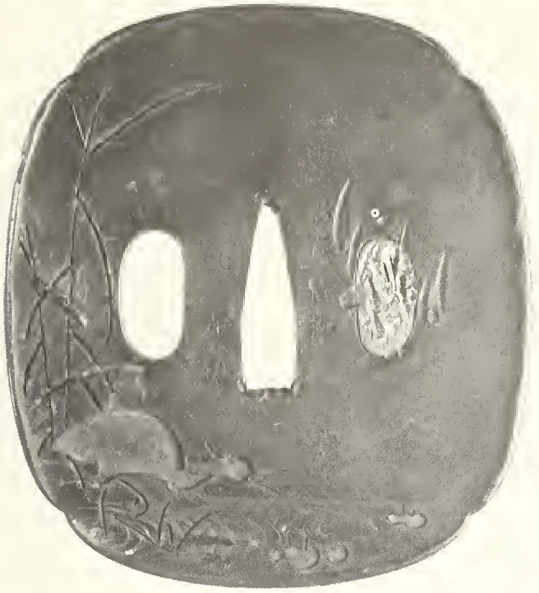
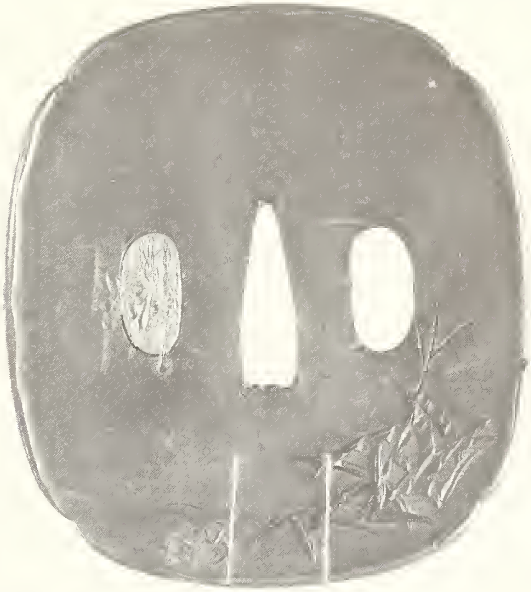

3a.
3b.
3c.
3e.
3d.
3f.

Fig. 3.—Tsuba no. 3. Brass, damaged. Signed "Shiunsai Hirochika." a. Obverse, natural size. b. Reverse, natural size, showing location of sections removed for analysis. c. Lower cross section, etched, ×1.5. d. Diagram showing location of photomicrographs on section 3c. e. Upper cross section, etched, ×2. f. Diagram showing location of photomicrographs on section 3e.

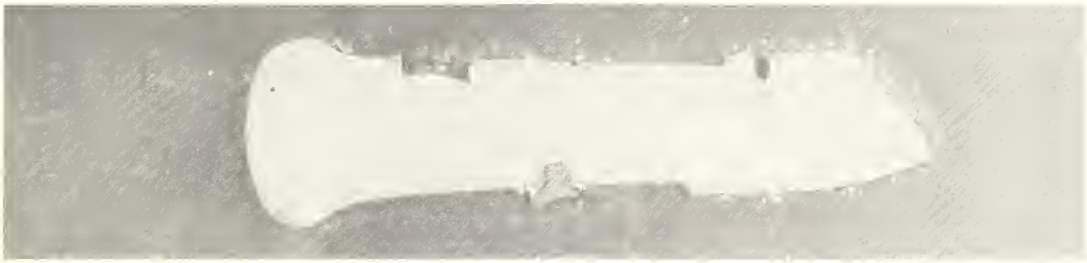
4a.



4b.



4c.



4d.

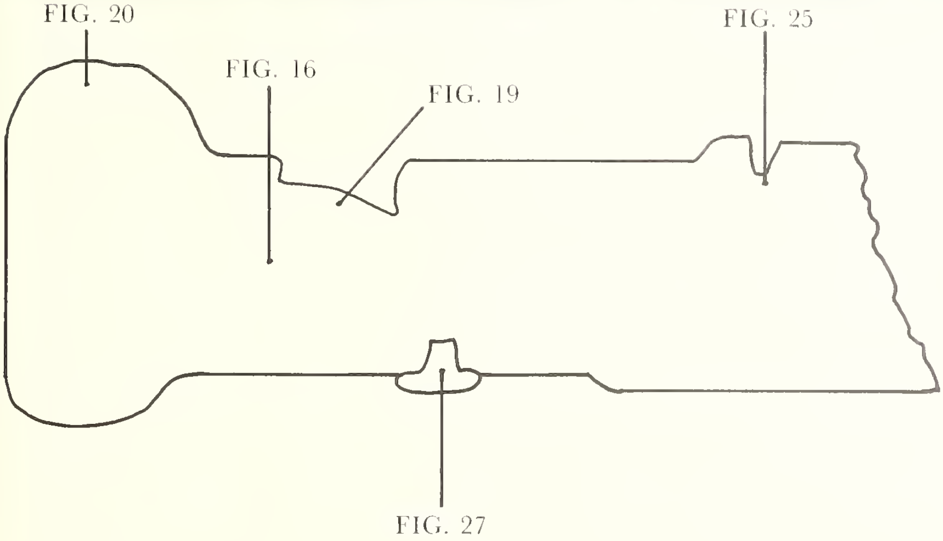
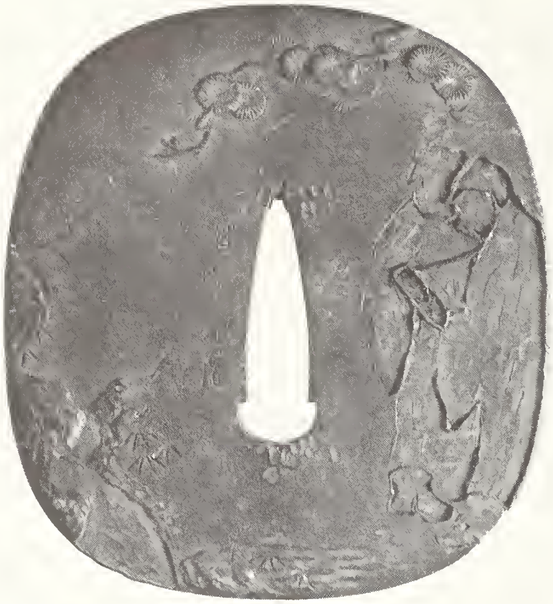
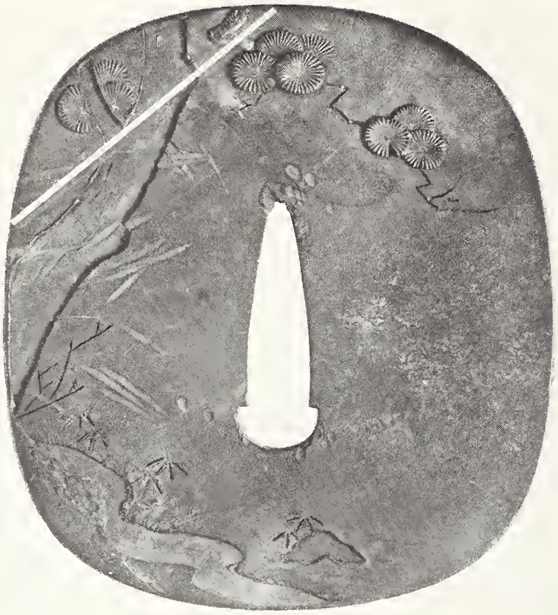


Fig. 4.—Tsuba no. 4. *Shibuichi*, damaged. Signed "Goto Hokkyo Ichijo." a. Obverse, natural size. b. Reverse, natural size, showing location of section removed for analysis. c. Cross section, etched, ×5. d. Diagram showing location of photomicrographs.

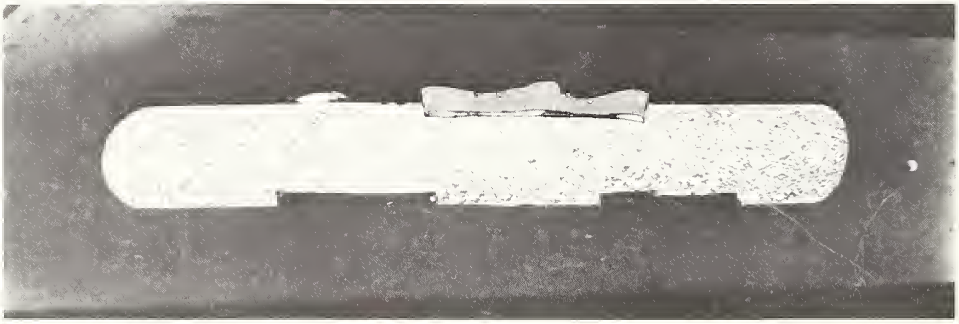
5a.



5b.



5c.



5d.

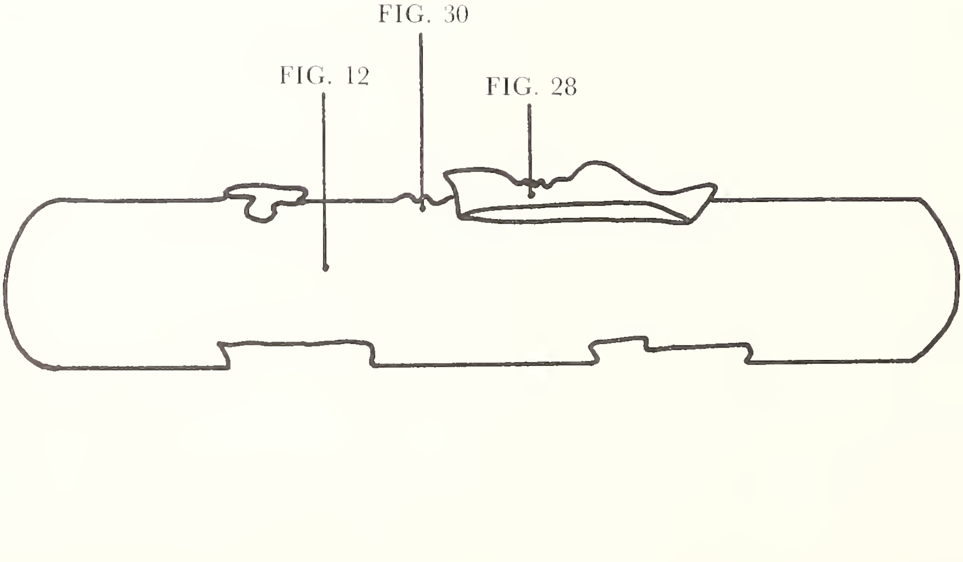


Fig. 5.—Tsuba no. 5. Brass, damaged. Signed "Hamano Noriyuki". a. Obverse, natural size. b. Reverse, natural size, showing location of section removed for analysis. c. Cross section, etched, ×3. d. Diagram showing location of photomicrographs.

Table 2

Chemical Composition and Hardness Measurements of Metals and Alloys

Tsuba No.	1			2			3			4		5		
Location of Sample	Body (percent)	Iron Inlay (percent)	Shakudō Inlay (percent)	Body (percent)	Iron Inlay (percent)	Shibuichi Inlay (percent)	Brass Body (percent)	Copper Inlay (percent)	Brass Inlay (percent)	Shibuichi Body (percent)	Shakudō Inlay (percent)	Brass Body (percent)	Inlay (Branch) (percent)	Inlay (Pine Cluster) (percent)
Copper	0.01–0.1	0.001–0.01	>90.0	0.01–0.1	0.01–0.1	P	66.4*	>90.0	>90.0	78.9*	>90.0	68.0*	>90.0	>90.0
Silver	<0.0001	—	0.01–1.0	—	—	>10.0	0.01–0.1	0.001–0.01	0.002	20.8*	>1.0	0.02	0.01–0.1	0.01–0.1
Gold	—	—	>1.0	—	—	—	0.05	0.001–0.01	0.001	0.06*	>1.0	0.0001–0.001	—	—
Zinc	—	—	—	—	—	0.04	32.3*	0.07	>10.0	0.3	—	31.1*	0.01–0.1	>1.0
Tin	—		0.02	—	—	0.04	0.2	0.01	0.1–1.0	0.05	0.02	0.08	0.002	0.2
Lead	—	—	0.04	—	—	0.05	0.1–1.0	0.1	0.1–1.0	0.2	0.01	0.3	0.08	0.6
Arsenic	—	—	0.01–0.1	—	—	0.001–0.01	0.01–0.1	—		0.01–0.1	0.3	0.01–0.1	—	0.04
Antimony	—	—	0.003	—	—	—	0.003	—	0.003	—	0.01	—	—	—
Iron	>90.0	>90.0	0.04	>90.0	>90.0	0.1–1.0	0.1–1.0	0.2	0.4	0.1–1.0	0.02	0.1	0.02	0.4
Nickel	0.001–0.01	0.001–0.01	0.01	—	—	0.03	0.02	0.02	0.03	0.04	0.02	0.1	0.02	0.08
Manganese	0.0001–0.001	—	—	0.0001–0.001	0.0001–0.001	—	0.003	0.0001–0.001	0.001–0.001	—	—	—	—	
Hardness (VHN)														
Range	118–202	138–212	134–166	104–206	176–247	151–186	111–132	59–62	97–135	118–173	123–187	78–103	56–69	87–104
Mean Value	158	168	152	145	199	165	119	60	118	139	159	85	62	97

Note—Unless marked (*) which designates wet chemical analysis, these are results of semi-quantitative spectrochemical analysis and give order-of-magnitude values only. A dash (—) indicates that the element in question was below the limit of detection, usually 0.001%. P indicates principal component. The microhardness tests were done with the Vickers diamond pyramid indenter, using a 300 gram load on all ferrous metals, 100 gram on copper alloys.

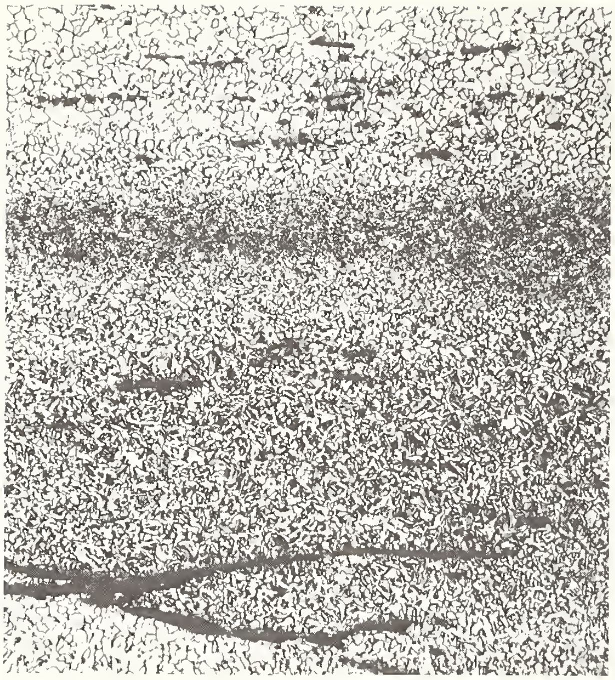


Fig. 6.—Tsuba no. 2. Section of body showing slag inclusions and wide local variation in grain size and carbon content. Nital etch, ×50.

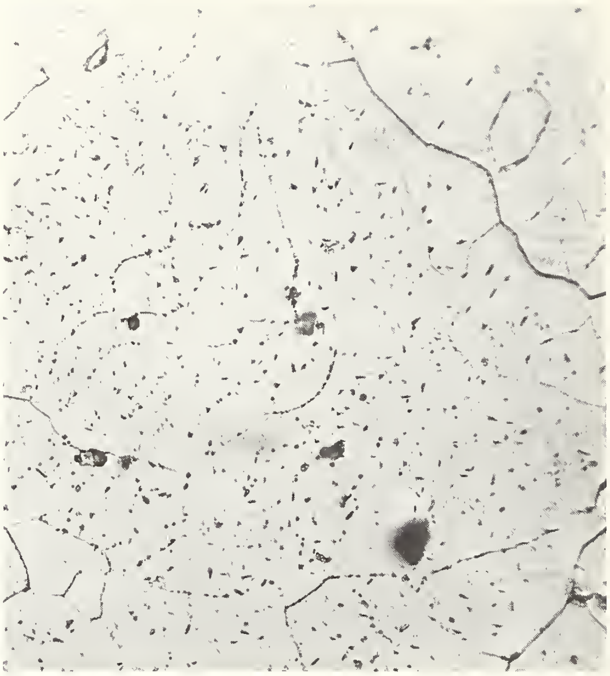


Fig. 7.—Tsuba no. 2. Photomicrograph showing inclusions, probably of iron nitride, in large ferrite grains in a carbon-free area. Nital etch, ×500.

fineness and distribution of the pearlite shows that the metal was cooled fairly fast, (probably in air, certainly not by quenching), from approximately 750–800°C. At high magnification (fig. 7), the grains in the carbon-free areas can be seen to contain many tiny, elongated inclusions, probably of iron nitride; nitrogen is frequently present in wrought iron made before the introduction of the puddling process.

It has been asserted by a leading authority[14] that *nambantetsu* was the superior high carbon cast steel, commonly known as wootz, made in India and exported for use in Damascus swords. This tsuba is certainly not made of wootz, unless the wootz had been so many times heated and rewelded by a Japanese smith that it had lost its carbon content and gathered an entrapment of slag. Instead, it is likely that the word *nambantetsu* was applied to many different grades of iron and steel. Wootz would be a good component of a forged sword, but its hardness would be of little advantage in a tsuba.

The iron in the Soten tsuba, Number 1 (figs. 8 and 9), was similar in general structure, but it contained less slag and fewer and smaller areas with visible carbide: the average hardness, however, was not significantly different.

As in all wrought iron, the slag in these two tsuba was distributed in long streaks resulting from considerable extension of the metal as it was hot-forged to shape from the initial sponge of reduced iron. The conspicuous bent-over streaks of high-carbon metal and slag in Figure 8 mark the end of a fold, probably formed by upsetting a taller chunk

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[14] H. L. Joly, "Note sur le fer et le style namban," *Bulletin Société Franco-Japonais*, 33 (1914), p. 1.

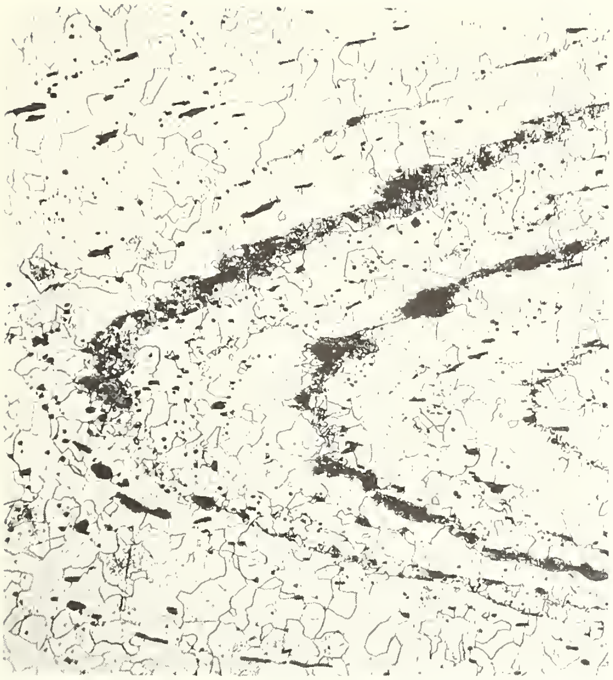

FIG. 8.—Tsuba no. 1. Photomicrograph showing streaks of slag inclusions and metal of different etching characteristics in a region near the edge, distorted by forging operation. Nital etch, ×50.

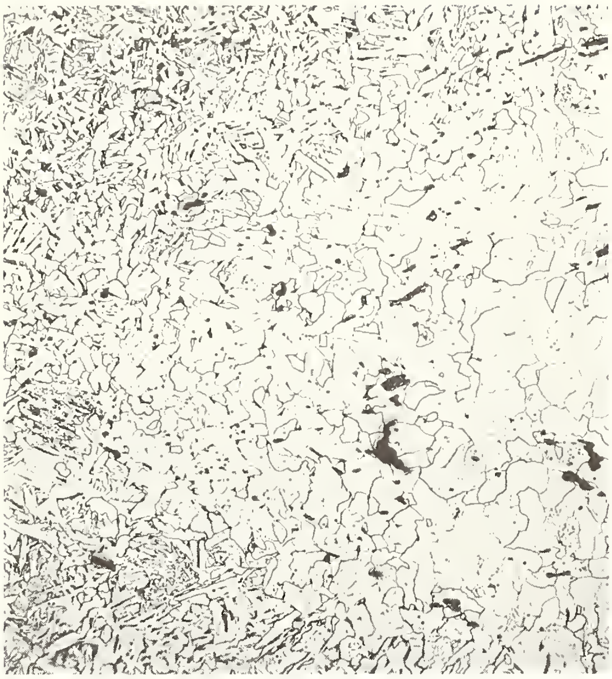

FIG. 9.—Tsuba no. 1. Photomicrograph showing transition between pearlitic and ferritic areas near external surface. Nital etch. ×50.

of iron into the flat disc from which the tsuba was carved, though it would be necessary to cut sections at different angles to completely establish the pattern of deformation. Note that in both the iron tsuba the slag particles are large and very irregularly distributed, not at all comparable with the fine dispersion of slag that is seen in the steel composing the outer parts of a Japanese sword, the metal for which is forged, folded, welded and extended many times under conditions of great cleanliness.

All forged iron has an internal texture that reflects and records both the initial heterogeneity of the iron as it aggregated in the smelter's hearth and the detailed history of subsequent welding and deformation. As with the grain of wood, fine patterns are revealed by cutting surfaces through it to intersect with the texture at various angles.[15] Though patterns of slag distribution can sometimes be seen on carefully polished surfaces of iron or steel, chemical etching produces more easily visible local variations in color, roughness, or level resulting from chemical heterogeneity, both in intentional constituents such as carbon and "impurities" such as nickel, copper, arsenic, or phosphorous. Such is the origin of the *mokume-hada* of the tsuba maker (fig. 10).

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[15] For a discussion of textured metals in general see C. S. Smith, *A History of Metallography* (Chicago: Univ. of Chicago Press, 1960), (Chapter 6 deals with Japanese swords and tsuba); C. S. Smith, "Sectioned Textures in the Decorative Arts," *Stereology*, Proc. Second International Conf. for Stereology, (New York, 1967), pp. 33–46; C. S. Smith, "Some Constructive Corrodings," *Corrosion and Metal Artifacts*, Brown, B. F., *et al.*, eds., U.S. Dept. of Commerce, NBS Special Publication 479, July, 1977, 143–153.

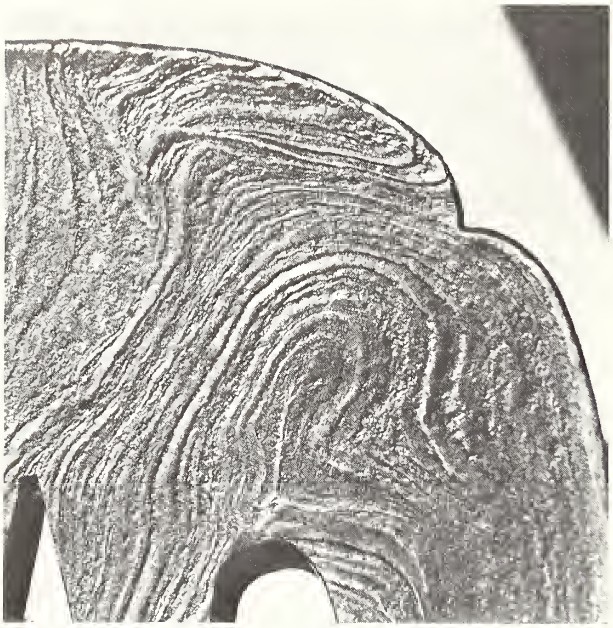

Fig. 10.—Tsuba, iron *mokume*, signed Kasaikei-en, mid-nineteenth century. (private collection). Detail × 1.5. The surface texture is the actual distorted grain of the metal developed by deep etching.

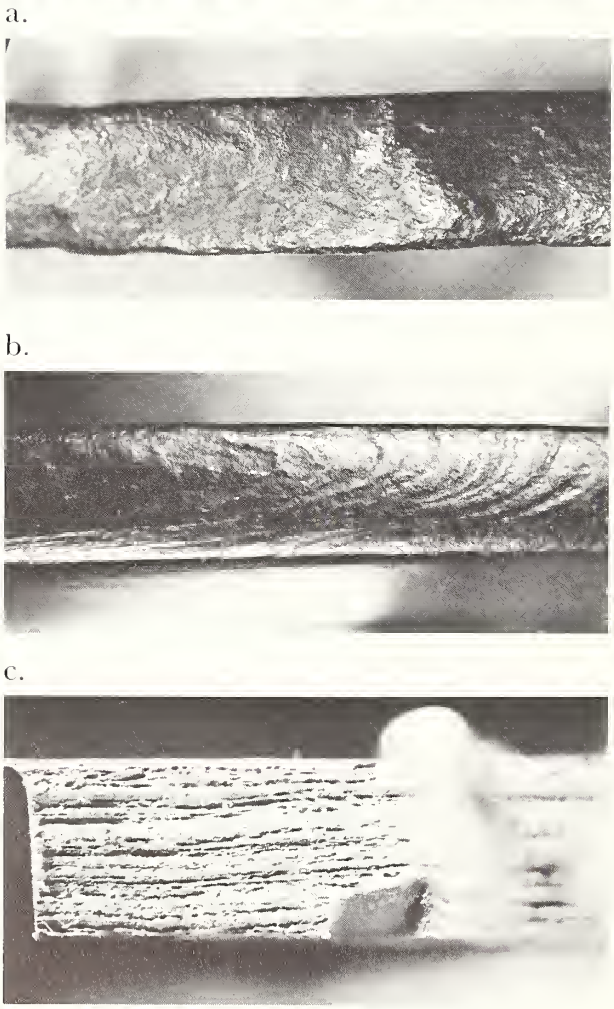

Fig. 11.—The edges of three iron tsuba showing the texture in the metal. a. Tsuba with irregular texture, mainly the result of natural corrosion and wear which has revealed the heterogeneity in the iron, "iron bones". × 5. MFA No. 13.2165. b. Tsuba having a *mokume* surface developed in relief by etching. × 5. MFA No. 11.11519. c. Tsuba no. 1. View of the side of the central hole (*nakago-ana*) which had been deeply etched by the vandals. × 6. Note the uncomplicated flat laminations in this iron, compared with the distorted grain in (b). The texture would not have been visible in the surface of the finished guard.

This effect is most beautiful when the texture arises principally from the natural flow of metal under the hammer, though contrived patterns in semi-geometric forms were often produced by welding together stacks or coils of composite or naturally heterogeneous metal. The surface before etching has to be cut below the outer surface left by the smith's hammer, and the most pleasing effects arise when the "grain" is sectioned at a glancing angle to enhance the irregularities, as in a beautiful wood veneer. (A cut at an angle of 6° to its surface magnifies the apparent thickness of a feature by a factor of 10, 1° by a factor of 50.)

Even when the texture on an iron tsuba has not been produced intentionally as in *mokume*, the surfaces of many of the older iron tsuba are rendered extraordinarily pleasing by the natural heterogeneities in the iron and consequent local variations in subsequent wear and environmental corrosion. The rims of old tsuba sometimes display the effect called "iron bones," *tekkotsu*, which mark underlying hard spots or lamellae in the metal (fig. 11a). This is sometimes faked by applied drops of cast iron.

MICROSTRUCTURE OF NON-FERROUS TSUBA

The analyses in Table 2 show that the bodies of tsuba Numbers 3 and 5 were of ordinary brass, *shinchū*, not the alloy *sentoku* which contains additions of both tin and lead. Nevertheless, these elements are present as impurities together with antimony, arsenic and iron, all of which would have some effect on the surface appearance and patination of the finished tsuba.

The microstructure of both brass tsuba (figs. 12 and 13) consists of equiaxed, twinned grains—the structure of metal that has recrystallized as a result of its being worked and annealed.[16] (These "grains" are the individual, randomly oriented crystals in the granular polycrystalline aggregate that makes up the piece. The word "grain" is also used, by analogy with wood, to refer to the lamellae and lines in the gross texture.) The average grain diameter of the brass is about 0.035–0.050 mm, corresponding to an annealing temperature in the range 525–575°C. The uniformity of the grain size suggests that the metal had been well worked before annealing, but sections of the guards examined after deep etching (figs. 3c and 5c) revealed ghosts of the dendritic structure of the cast metal without extensive distortion, which make it clear that the castings could not have been more than about twice the present thickness, and they had been hammered no more than enough to consolidate minor porosity.

The tsuba made by the eminent Goto Ichijo (no. 4), is of *shibuichi*, the alloy unique to Japan that contains between 20 and 50% silver, the balance being copper. In this tsuba the silver content is at the lower limit, but enough is present to form a network of the separate, finely duplex microconstituent (called a eutectic) containing 72% silver which surrounds the copper dendrites and contributes to the unique surface qualities of the alloy. The scale of the silver network in this tsuba is very fine—much finer and more uniform (less dendritic) than we have been able to duplicate in castings of the alloys in the laboratory. The texture due to this network of silver is just discernible in the upper

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[16] Unless otherwise noted all non-ferrous microsamples were etched with an aqueous solution containing 2% potassium dichromate, 1.5% sodium chloride and 10% sulfuric acid.

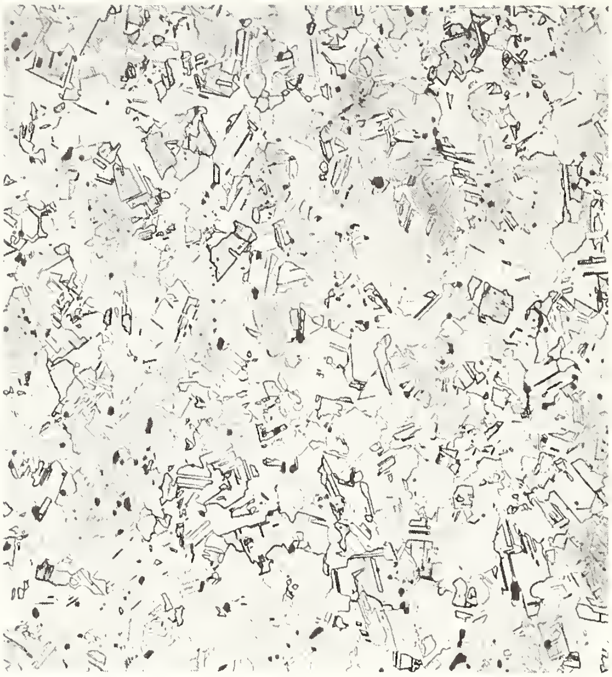

Fig. 12.—Tsuba no. 5. Microstructure of section showing twinned, approximately equiaxed, grains of irregular size resulting from cold working followed by annealing. The black spots are non-metallic inclusions that were present in the metal when it was cast. Etched, × 100.

portion of Figure 14, which shows the original surface at a magnification of 9 × . Figure 15 shows the structure in another tsuba more clearly resolved at higher magnification. The duplex structure can rarely be seen with the unaided eye, but nevertheless it is responsible for the finely matte surface and the variations of color and quality of light scattered at different angles of observation. Also, since the silver remains slightly in relief after the final pickling operation which colors the copper, the appearance of the surface is relatively unaffected by ordinary wear.

As with the brass tsuba, the dendritic structure of the cast *shibuichi* is preserved, although distorted. The anisotropy of the microstructure in the cross section (fig. 16) is about two, corresponding to a reduction of thickness (if by uniform compression), of about 35% from the original casting. That this reduction was not done by unidirectional rolling is shown by the isotropy of the structure when viewed on the surface of the tsuba (fig. 15): the hammering has extended the metal uniformly in all directions, essentially magnifying the gross texture without distorting it. (Such extension occurs only in the plane normal to the direction of compression, and it is necessary to examine the texture of sections cut in more than one orientation if the nature of working of a piece of metal is to be unequivocally determined).

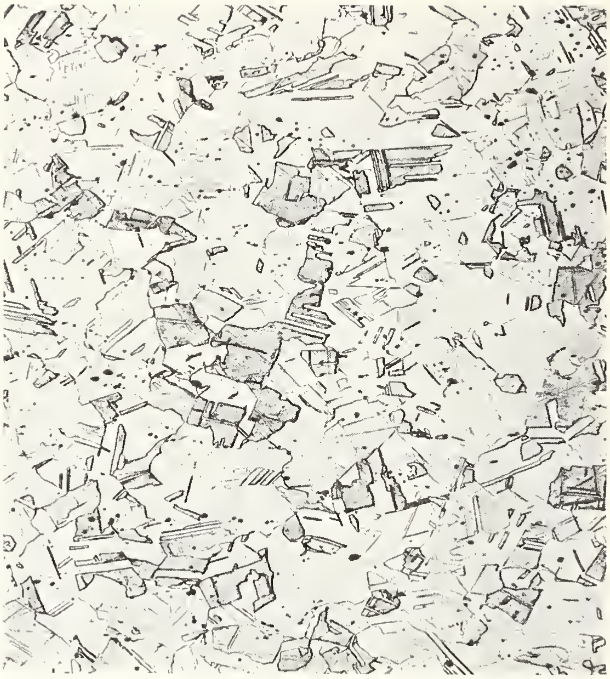

Fig. 13.—Tsuba no. 3. Microstructure showing twinned equiaxed grains, somewhat larger than those in figure 12. Etched, × 50.

In the tsuba that were examined microscopically *shakudō* was used only for inlay. Although this is a single-phase, solid solution alloy, there is sufficient segregation during

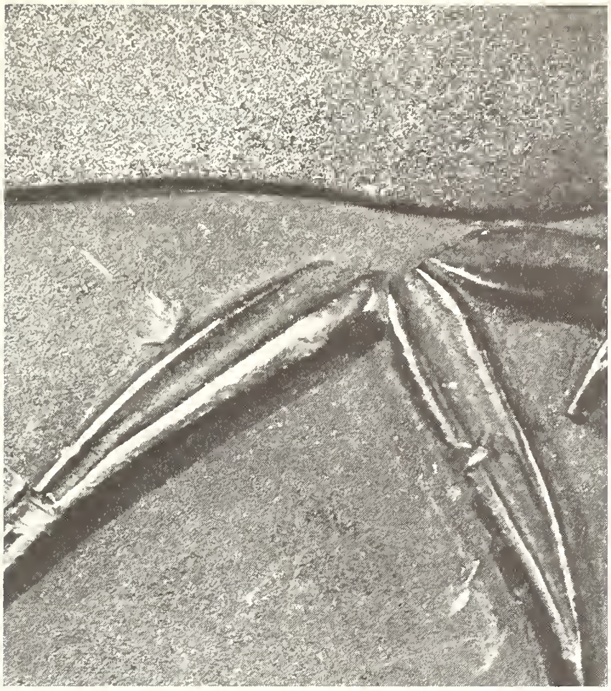

Fig. 14.—Tsuba no. 4. Detail of surface, ×9. Note the just-visible texture of the *shibuichi* in the area at the top. The area below, though of the same metal, is rougher and darker in color, indicating that the upper part had been re-polished prior to the final stage of a long patinating treatment.

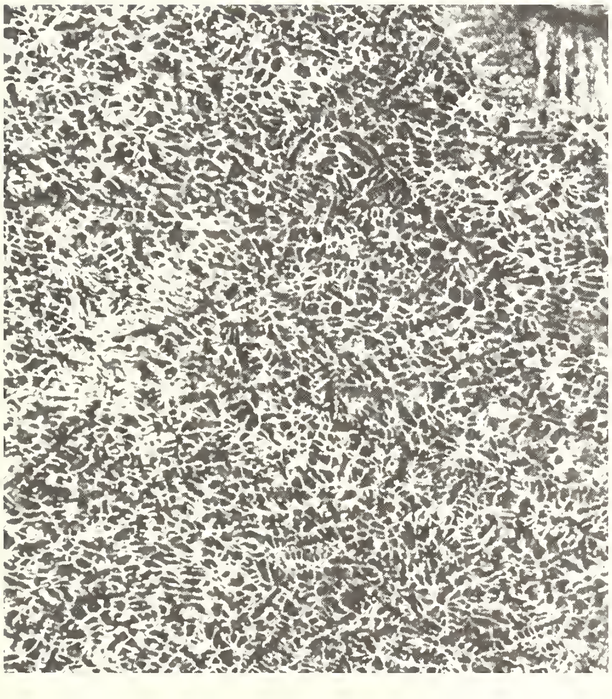

Fig. 15.—Untouched surface of *shibuichi* showing the natural surface as finished by the maker. The fine silver network (which is unusually coarse) stands slightly proud above the darkened, copper-rich areas. The engraved line is part of the maker's signature. ×15. MFA No. 21.727.

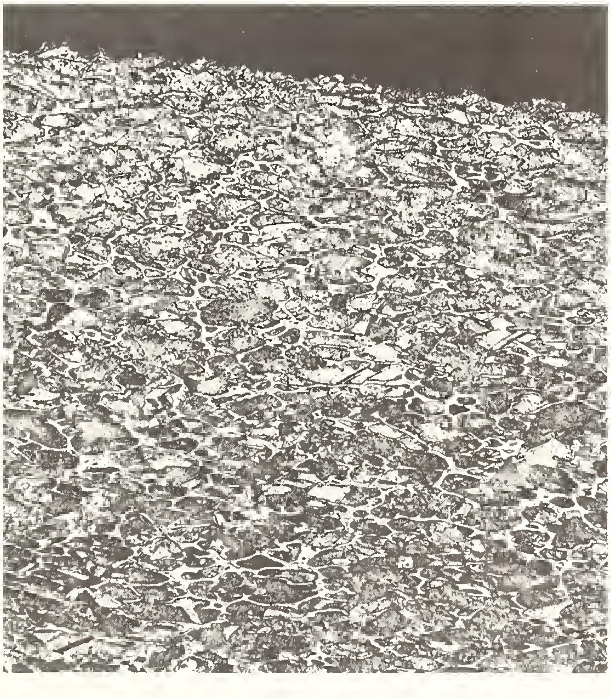

Fig. 16.—Tsuba no. 4. Microstructure of cross section of *shibuichi* showing a white, distorted network of silver surrounding the copper-rich grains with graded dark stain. ×200. Compare with Figure 15 which shows a similar structure as it appears on the original finished surface of the tsuba. The anisotropy in the section naturally accompanies the reduction of thickness of the metal by hammering.

the solidification, especially when silver is present, to produce etchable differences in color. As one would expect from the small sizes of the inlaid pieces, there has been considerable distortion of the cast structure due to the shaping (see figs. 26 and 27). The sections are lath-like rather than fibrous, showing that the little strips for inlay were cut from a sheet hammered to the appropriate thickness, not made from wire that had been drawn through a die.

CARVING TECHNIQUES

Many beautiful early iron tsuba are decorated by simple perforation through the uniform thickness of a disc of metal, the design being in negative silhouette. In these, as in the later more elaborate *kio-sukashi* tsuba with figures in slim positive silhouette with the background entirely cut away, the technique involved nothing more complicated than drilling, sawing, and filing. Most tsuba however, have features in three-dimensional relief, finished by carving. The design can stand proud above the main level of the tsuba surface, be in shallow sunk relief, or be in full relief within the thickness of the tsuba. *Marubori* (also called *nikubori-sukashi*) is the technique of carving in the round, within the tsuba thickness, with the background cut away. Such work is also used as a basis for inlay and encrustation with colored nonferrous metal details and is represented among our samples by one of the elaborately carved and decorated tsuba of the Soten school of Hikone (no. 1, fig. 1). This had been very deeply corroded in acid by the vandals in an attempt to remove the gold inlay and *nunome* overlay. The original carved surface was totally destroyed, but the etching served to reveal the grain of the metal very clearly, both roughening the surface and penetrating along the slag locations. The parallel continuity of the grain (fig. 11c) made it evident that the disc had been cut from a larger flat piece of wrought iron with a generally lamellar texture, and that, after forging, it had been cut to its final shape without further deformation of the metal. The microstructure of the transverse section (fig. 26) shows the horizontal grain extending undisturbed to the surface of the shaped details.

INLAY TECHNIQUES: ZŌGAN

Japanese tsuba makers are famous for their inlay techniques. Although in early tsuba the grooves were made by tracing and were so shallow that the inlay has often become detached (fig. 17), in later work the grooves were deeply and cleanly cut and the attachment secure. In the damaged tsuba that we studied, much of the inlay had been pried out and the details of the prepared cavities could be clearly seen. Two kinds of true inlay, *hon-zōgan*, were represented: the rather large shaped areas of relief inlay and flat inlay, *uttori-zōgan* and *taka-zōgan*, respectively, set into wide cavities cut into the base metal; and the narrow linear decoration, *sen-zōgan*. The appearance of a typical chiseled-out cavity for *uttori-zōgan* in the Hirochika tsuba (no. 3) is shown in Figure 18 and in a cross section of the cavity in another tsuba in Figure 19. Note, in the latter, the relatively undistorted metal left beneath the chisel cuts at the bottom of the cavity (evidence of an exceedingly sharp chisel), and the distortion and recrystallization at the side where

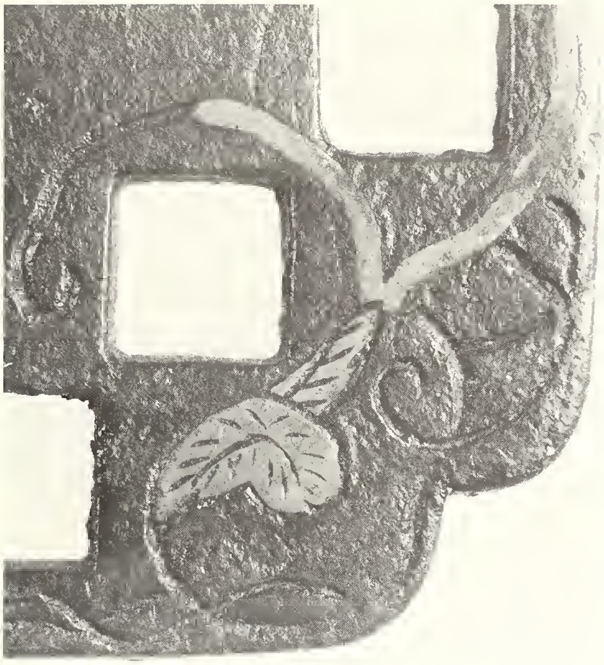

FIG. 17.—Iron tsuba with brass and copper inlay. *Heianjo* style, late sixteenth century. ×5. The grooves for the inlay were traced and are too shallow to secure the inlay, some of which has become detached. Private collection.

the base metal has been displaced in the final operation to secure the inlay. In the Ichijo tsuba, seen in cross-section in Figure 20, the edge of the cavity shows relatively more flow of metal and the amount of overhang at the edge of the cavities is less than expected. At least in the place sectioned, the accuracy of fit and lateral compression were more responsible for securing the inlay than simple mechanical interlock. That it was effective is demonstrated by the fact that the joins are not visible on the surface of the tsuba and there is no local damage to the surface caused by seepage of the solutions used in patination.

In the Noriyuki tsuba, Number 5, a large inlaid piece had been additionally secured by a small blob of soft (lead-tin) solder, localized at one corner. There was, however, no evidence of the use of solder in the other tsuba, and it would serve no purpose in true inlay if the fit were good.

Figure 21 shows the narrow inlay representing the bamboo table legs of the Hirochika tsuba (no. 3). In cross section (figs. 22 and 23), the result of using a flat-ended punch and a tracing tool to define the outline while securing the piece is evident.

Figure 24 shows, at low magnification, an area of the Ichijo tsuba (no. 4) from which narrow relief-inlay details have been stripped by the vandals. The deep chisel marks at the bottom and traces of the blunt punch or tracing tool used to crimp the surrounding metal after the inlay had been placed are both visible. In the finished tsuba this would have been hidden by spreading over of the inlay, perhaps resembling that in Figure 14. The narrow grooves for this type of inlay were made in two different ways, either by cutting out metal with a narrow chisel or graver, or by punching deeply with a tracing tool. Both techniques were used on this tsuba, although on opposite sides. The difference is clearly seen in the cross section (figs. 19 and 25). The extensive flow of metal caused by the punch and revealed by the distortion of the grains of the adjacent metal in the latter should be compared with the abrupt termination of the undeviated grain at the side of the cut in the former.

The clean intersection of the cut groove with the grain of the metal is seen even more clearly in the Soten tsuba (fig. 26). The contrast should be noted between the deformation patterns in the iron base metal and that in the inlay, revealed by the grain in their respective structures. The iron had been cleanly cut to form the cavity, leaving its grain without distortion, in contrast to the distortion of the inlay strip. From this, one

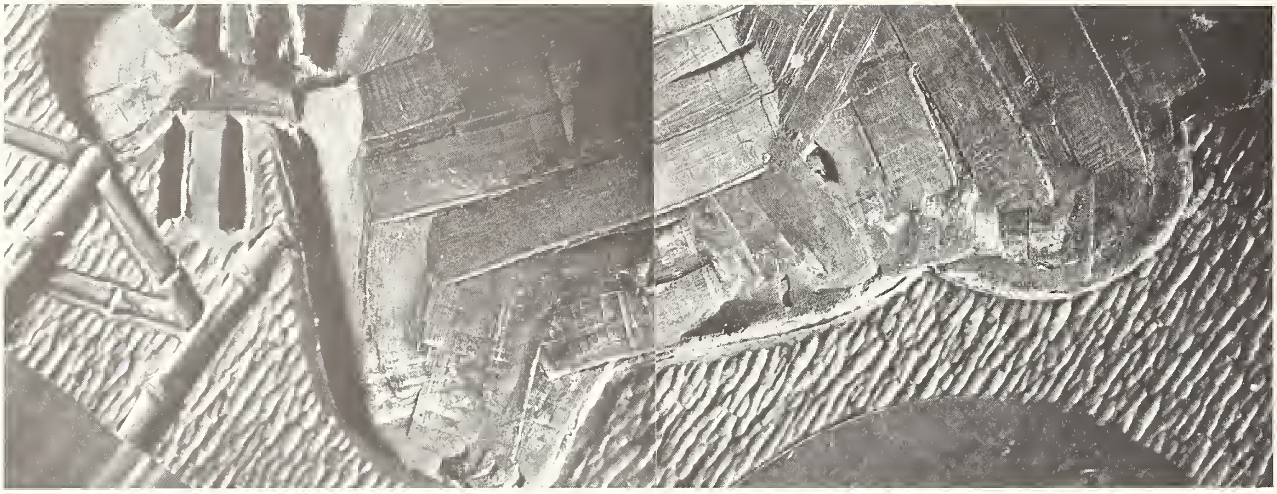

Fig. 18.—Tsuba no. 3. Photograph showing chisel marks in bottom of cavity cut to receive inlay. ×9.

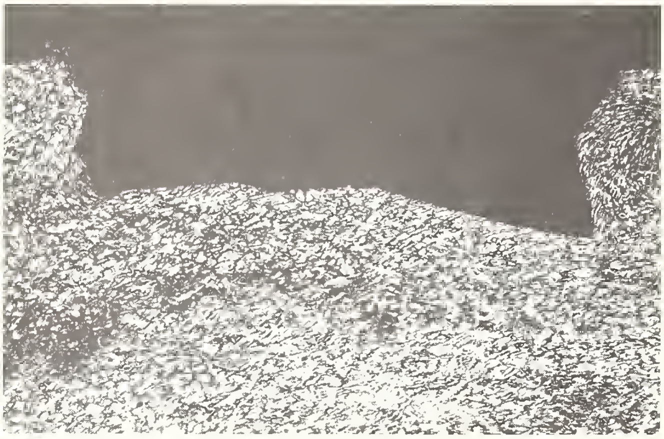

Fig. 19.—Tsuba no. 4. Cross section showing the cavity cut to receive the inlay. Etched, ×37.5. Note the clean cut at the bottom and the distortion of the metal at the edges which had been compressed to secure the inlay.

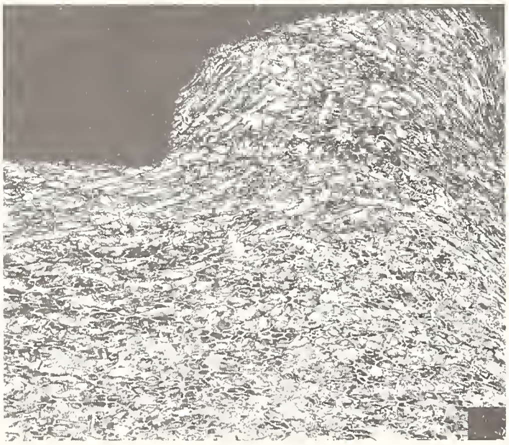

Fig. 20.—Tsuba no. 4. Section through area near rim. Etched, ×33. Note how the metal had been distorted by lateral hammering to provide a local increase in thickness, although the final contours of the inside of the rim have been carved, intersecting the metal texture.

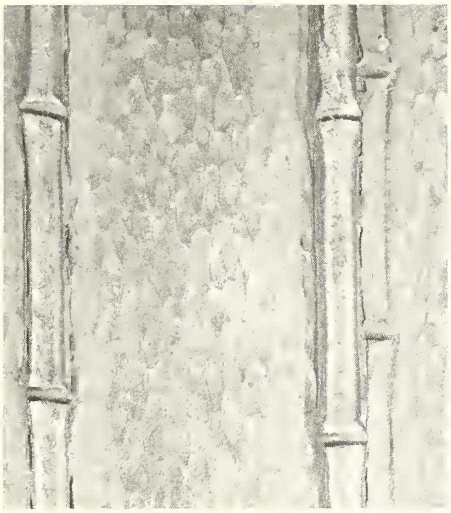

FIG. 21.—Tsuba no. 3. Detail showing surface texture produced by punching and the relief inlay of the bamboo table legs (see Figure 3(a)) ×6.5.

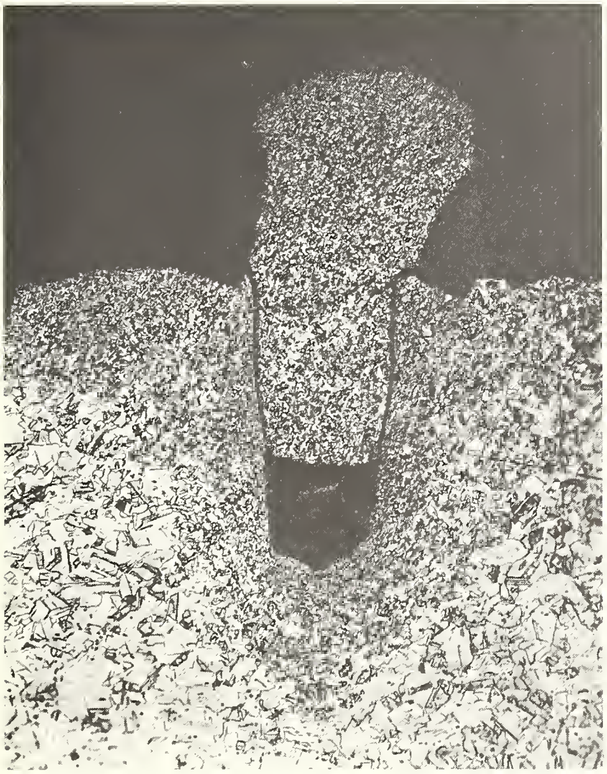

FIG. 22.—Tsuba no. 3. Section through the right "bamboo" inlay shown in Figure 21. Etched, ×46. Note the fine recrystallization around the groove extending onto the surface at the left, which is an area of the base metal worked to represent the partly-hidden rear leg.

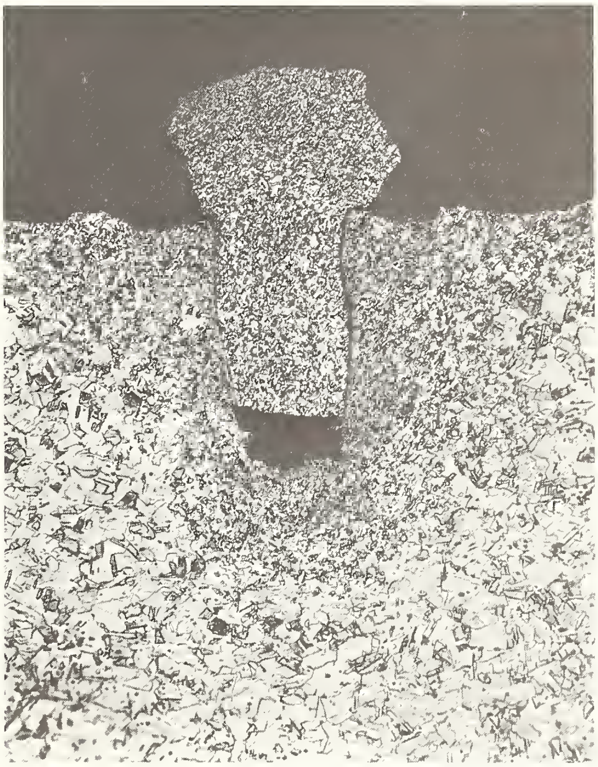

FIG. 23.—Tsuba no. 3. Section through the "bamboo" inlay on left of Figure 21.

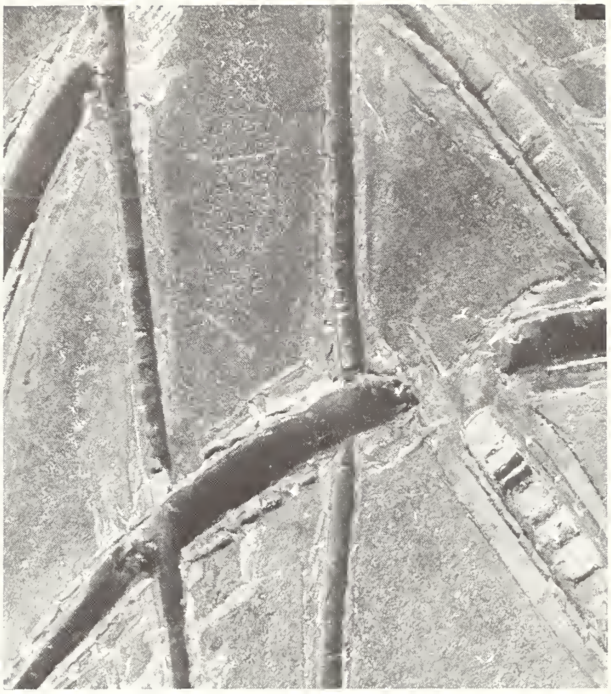

FIG. 24.—Tsuba no. 4. Surface, showing chiselled grooves from which the inlay had been forcibly removed by the vandals. ×9.

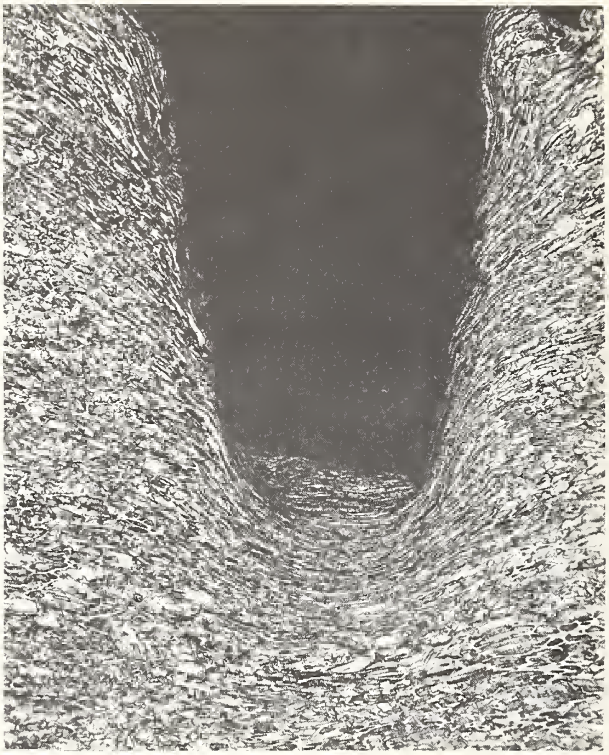

FIG. 25.—Tsuba no. 4. Cross section of groove for inlay. Etched, ×88. Note the flow of metal near the sides of the cavity, showing that the groove had been made by displacing the metal with a narrow, blunt punch or tracer, not cutting it away with a chisel. Compare with Figure 27 showing a groove made by cutting, on the opposite side of the same tsuba.

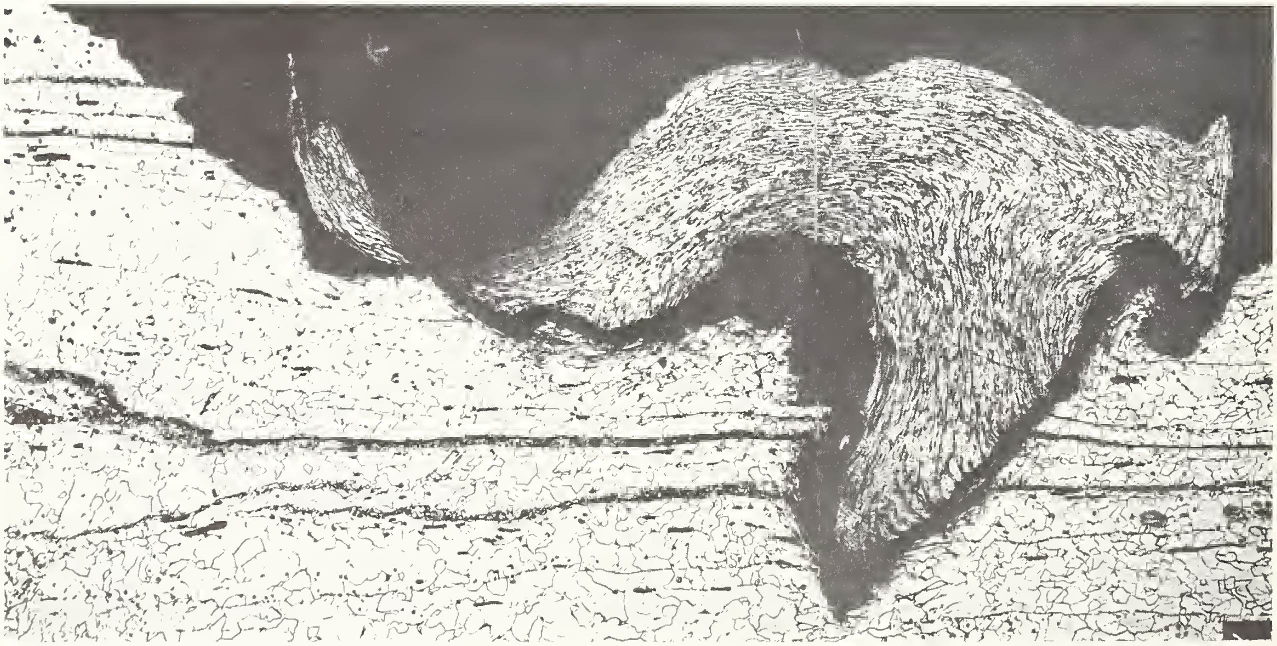

FIG. 26.—Tsuba no. 1. Section, showing inlay. Etched, × 50. Note the abrupt termination of the grain of the iron base metal at the carved surfaces and the pattern of distortion in the *shakudō* inlay.

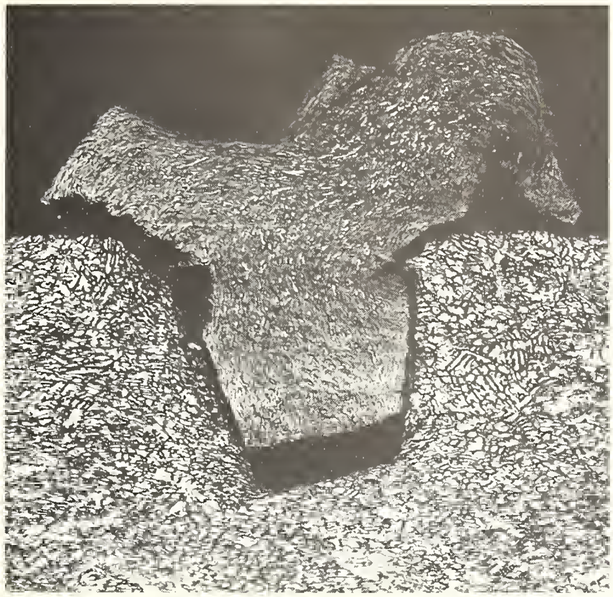

Fig. 27.—Tsuba no.4. Section through *shakudō* inlay. Etched, ×44. Note the lack of local deformation in the base metal alongside the groove, which had been chisel-cut, not punched as in Figure 25.

can deduce that the inlay has been partly cut to shape from a hammered strip, inserted edgewise into its groove, then secured by striking the adjacent edge of the iron with a tracer and finally shaped by upsetting the inlay over the iron, tracing and chiselling to achieve the desired shape.

Figure 27 is a cross-section of a similar feature made of *shakudō* inlaid in the *shibuichi* body of the Ichijo tsuba. In the original piece this inlay formed a leaf identical with those shown in Figure 14. The grooves in Figure 24 are in an adjacent area stripped of inlay.

The above discussion concerns the inlaying of details composed of a metal different from that of the ground, which is, of course, the usual function of inlay work. A rather unexpected finding was that in both the iron and nonferrous tsuba there were areas of relief inlay made of the same metal as the base and externally appearing to be integral with it, as if the relief had been achieved by carving away the surrounding metal in a thicker, solid block. Examples are the iron fisherman's body in Number 2, the clusters of pine needles in Number 5, (made of brass) (fig. 28) and the upper part of the tree trunk in the Soten tsuba, Number 1. The last is most remarkable, for the iron inlay has been carved to form a feature entirely below the main surface of the disc of metal from which the tsuba had been carved; it could more easily have been made integrally with the rest of the guard, with which it is identical. Supposedly it had been inserted to rectify a mistake in carving, or perhaps to replace a local area of defective, slag-rich metal. In other cases where inlay of the same metal was applied, it was in relief, above the main surface, suggesting that the technique was used to simplify the shaping

Fig. 28.—Tsuba no. 5, showing detail of inlaid pine needle cluster. The inlay is of the same metal as the tsuba body. The surface has been shaped by both deformation and carving. Etched, ×50.

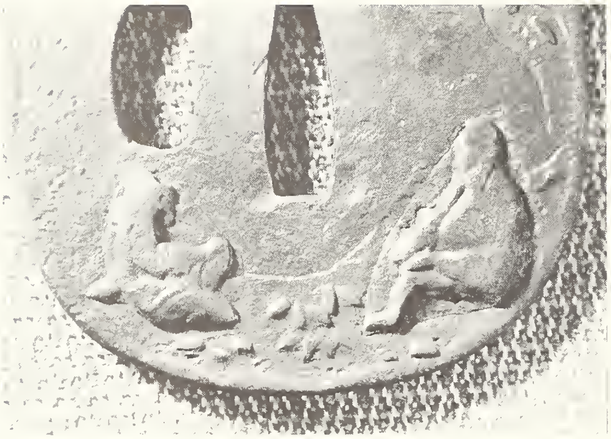

Fig. 29.—Iron tsuba, × 1.2, with relief figures formed as part of a large inlaid piece extending into the neighboring flat ground of the same material. The line of junction would originally have been invisible, but it was exposed by a deep pickling followed by wire-brushing. The J. W. Higgins Armory, Worcester, Massachusetts.

process. A disc of metal could be forged, filed or abraded to a flat surface and then inlaid with local features in relief far more easily than the same design could be realized by forging a piece with varying thickness or by making a thick uniform blank and carving away a great mass of solid metal to leave a few protuberances. The technique is somewhat analogous to the assembled wood-block construction introduced by Japanese sculptors during the Heian period, which influenced both the form of the product and the organization of the workshop.[17]

So exquisitely are the inlays fitted and finished that there is no external hint of the presence of a joint unless the metal is of a different color. The outline of the cavity for the inserted piece does not need to coincide with that of the relief figure on the finished piece but sometimes extends into the flat ground since the patination serves to hide the joint. The line, however, can be seen on a tsuba in the Higgins collection (fig. 29) which has been deeply pickled in acid and scratch-brushed in a misguided attempt to clean it.

In some tsuba, a wide rim (*dote-mimi*), thicker than the body of the tsuba, is produced by carving away most of the inner surface of the blank. More common is the *ukikaishi-mimi* in which the metal has been deformed by hammering on the edge after the main surface has been shaped. The highly raised rims that appear on some of the early iron tsuba made by armorers suggest the use of heavy blows on hot metal held in a vise-like anvil with curved jaws, while the rims of two of the nonferrous tsuba used in the present study appear to have been formed by many light, fast blows on the unsupported edge of the metal disc. The inevitable variation between individual hammer blows produces a very beautiful effect, with upturn and local curvature reflecting the way in which the metal has flowed. Figure 20, a cross section through the Ichijo tsuba, illustrates the flowed and upset grain of the metal clearly, although some final shaping had been done by cutting.

It is likely that the inlaid pieces would have been roughly shaped prior to insertion in the prepared cavities and given their final details by chiseling, chasing and tracing after securing in place. The final surface prior to chemical patination was achieved by abrasive powders on a hard backing or with abrasive stones, leaving the surface almost geometrically smooth and with a finely matte quality. The most magnificent results of such polishing techniques are to be seen on Japanese sword blades. These techniques were used on bronze ceremonial objects at least as early as the Nara period and they were derived, of course, from those used in finishing jade many centuries earlier in China. The surface quality of Japanese polished metal is quite different from the brutally buffed and burnished finishes of Western metal work in which the metal has been caused to flow superficially; the graded abrasives leave the true structure of the metal virtually undistorted. Scientists in the West were unable to see the true microstructure of metal until they had developed methods of both polishing and etching much like those used by the tsuba maker.[18]

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[17] It should be noted that both relief inlay and cutaway-ground techniques were used by Sasanian silversmiths to give figures in relief. See O. Grabar, "An Introduction to the Art of Sasanian Silver," *Sasanian Silver* (catalogue for an exhibition) (Ann Arbor, Michigan: Univ. of Michigan Museum of Art, 1967), p. 19 ff. Except for that of Mycenaean smiths (see R. Laffineur, "L'Incrustation à l'Epoque Mycenienne," *l'Antiquite Classique*, vol. 43 (1974), pp. 5–37) Sasanian work in colored metals is the only kind that bears technical comparison with that of the Japanese.

The fine recrystallization observed on the brass tsuba in areas that have been locally worked shows that they have been given a low temperature annealing treatment (a few minutes at a temperature of approximately 400°C) after the working had been completed. (See Figure 30 which is a section normal to the surface of Number 5 and illustrates the structure resulting from an *ishime-ji* finish, formed by innumerable blows from a rounded punch. The recrystallization of the distorted metal immediately underlying each punched depression is indicative of the effects of heat treatment. The finish is illustrated in Figure 21). Whether such heating was done by the original maker or by the vandals in their attempt to remove the gold cannot be ascertained. The surface of Number 5 was irregularly and heavily oxidized, including the areas from which the inlay had been removed, indicating that heating in this case had been done by the vandals. However, low-temperature heating was usually a part of the patination process as well as being necessary in gilding, such as that applied to Number 3. Moreover, heating after inlaying could have been done by the maker to better secure the inlay to the base metal.

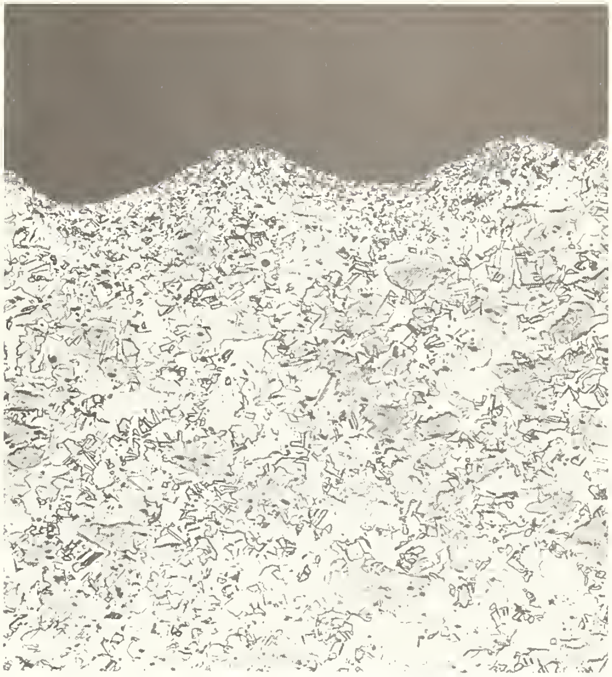

FIG. 30.—Tsuba no. 5, cross-section through area immediately adjacent to Figure 28, in which the pine needles were shaped with a punch, not carved or inlaid. Subsequent heating has caused fine recrystallization in the heavily deformed metal at the surface. Etched, ×50.

Nunome, sometimes called false inlay to distinguish it from the deeply inserted pieces discussed above, is a method of attaching superficial decorative detail by hammering gold or silver wire or foil on to a surface (usually iron) that has been roughened to provide mechanical interlock on a microscopic scale for the softer precious metal. The surface is most commonly prepared by cross-hatching with a sharp chisel to produce a texture not unlike that of a file surface, though

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[18] Smith, *A History of Metallography*.

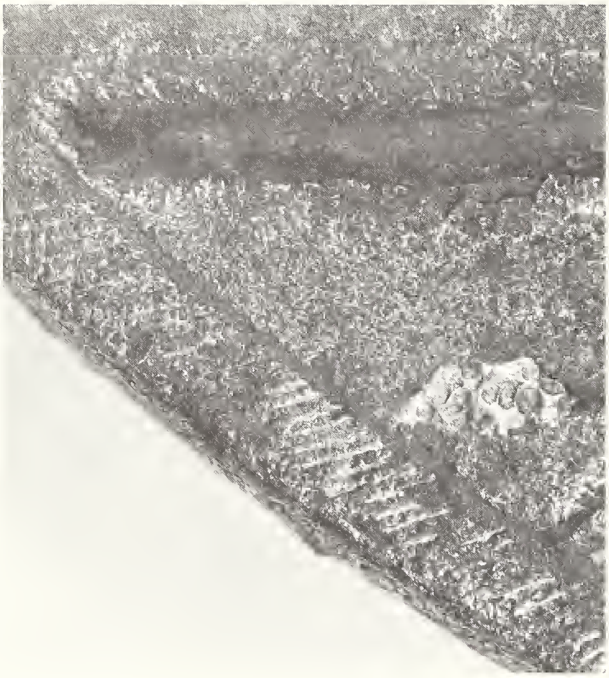

FIG. 31.—Tsuba no. 2. Rim shows area of *nunome-zōgan*, worn and corroded so that the gold remains only in the bottom of the shallow grooves cut to retain it. × 10.

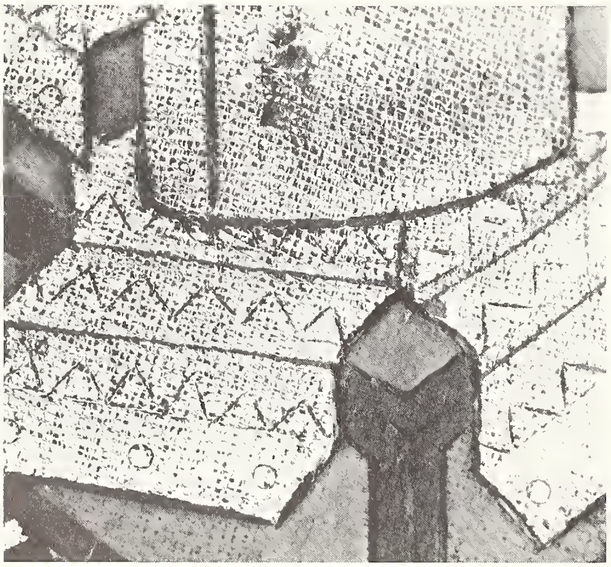

FIG. 32.—Tsuba, the surface of which is entirely covered by *nunome-zōgan* in metal of six different colors. Detail, × 5. MFA 07.882.

the Japanese name refers to the weave of a textile. Metalworkers today use chemical action to enhance the roughness and often produce it entirely in this way. In many old tsuba the *nunome* remains only as cross-hatched lines, since the previous metal layer has been removed by wear. In Figure 31, for example, the gold that now forms inconspicuous lines had originally covered the entire rim. An impressive example of *nunome* is the tsuba in the Museum of Fine Arts, Boston, in which the entire surface is covered by a design incorporating foils of metals of several contrasting colors. A detail is illustrated in Figure 32.

A fine contrast with the black surface of iron is provided by inlay with *sawari*, which is a hard, brittle white alloy of copper and tin approximating speculum metal in composition (about 33% tin, melting point about 750° C).[19] Unlike other inlay, *sawari* is not mechanically attached but is melted to fill in the engraved lines and chiselled-out recessed areas. The surface of the object is thereafter polished and ground flat as in *taka-zōgan*, but it is more like niello or champlevé enamel. The inlay, initially mirror-bright and tarnish-resistant, does slowly turn grey with age. Since

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[19] The high-tin bronze that was used in the Nara period to make ceremonial vessels (for example, those in the Shōsōin) is also sometimes called *sawari*, but this is less brittle and much less white than the alloy of the fused-in inlays. Though we have seen no analyses, we suspect the vessels to be of the 23% tin alloy used in Persia for similar purposes at about the same time and which has a long history of use in Southeast Asia, especially in bowls and gongs. Unlike bronzes with substantially higher or lower tin content, this alloy is extremely malleable when hot and is easily forged to shape above about 550° C. However, it must be rapidly quenched if it is not to become brittle at room temperature. In this condition it is readily identified by its unusual microstructure, called "martensitic" by metallurgists.

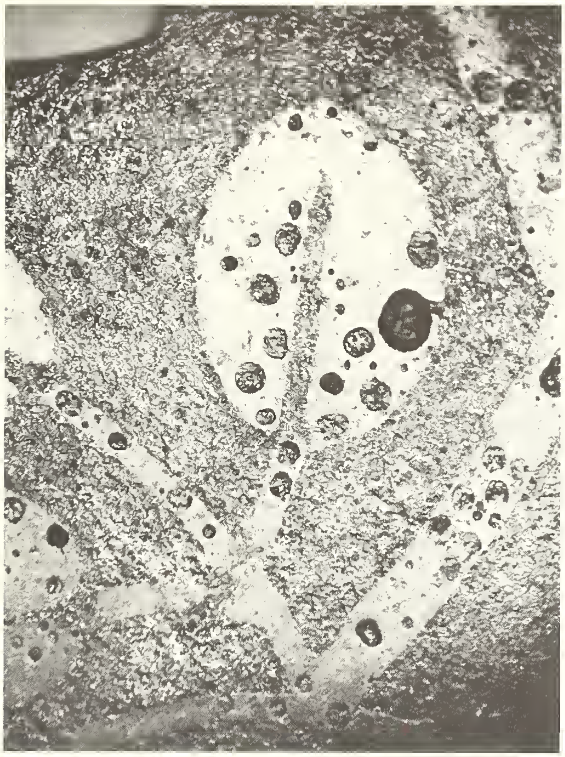

FIG. 33.—Iron tsuba with leaves depicted in *sawari* inlay. Signed "Teiei". Detail × 5. MFA 13.2057.

sawari is a brittle alloy, large areas of it often contain cracks. Some gas bubbles are present even in the best work and serve to relieve the monotony of the rather hard surface as well as identify the alloy. In the tsuba shown in Figure 33, there are more bubbles than usual. X-ray fluorescence analysis confirmed that this example is a nearly pure copper-tin mixture. More complex alloys have been mentioned in the literature, including *shirome*. This is a speisse containing arsenic and antimony, obtained as a by-product from the desilvering of copper by liquation. This was used as an alloying addition in copper to modify the patina quality, but we have not seen any example of its use as an inlay.

Another once common technique involving fused metal is *gomoku-zōgan*, "dirt" inlay, or more accurately, overlay. In this technique an irregular array of pieces of brass (wire or clippings) is secured to the surface of an iron tsuba by a brazing solder of high zinc content or, possibly, *sawari* (fig. 34). In *suemon-zōgan*, (a technique used most effectively by Shimizu Jingo and his followers, as well as by the Yanagawa school), large well-shaped areas of brass bearing a relief design are attached by soft solder to the surface of an iron tsuba without the excavation of the ground. Since the solder remains invisible, the effect closely resembles *uttori-zōgan* but is subtly different in the definition of the edges of the applied piece.

In the techniques just mentioned, the molten metal must wet the solid metal beneath it and spread by capillary action over its surface.

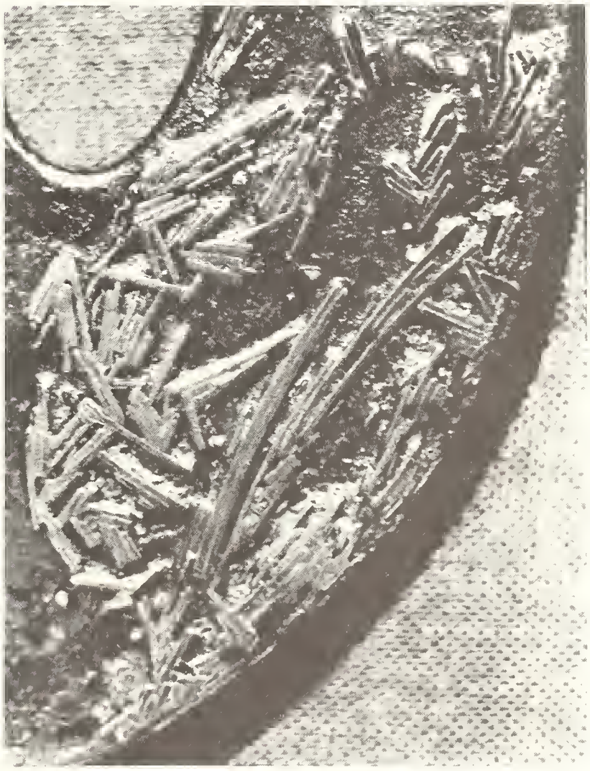

FIG. 34.—Tsuba decorated with *gomoku-zōgan*. Detail, × 5. MFA 06.187.

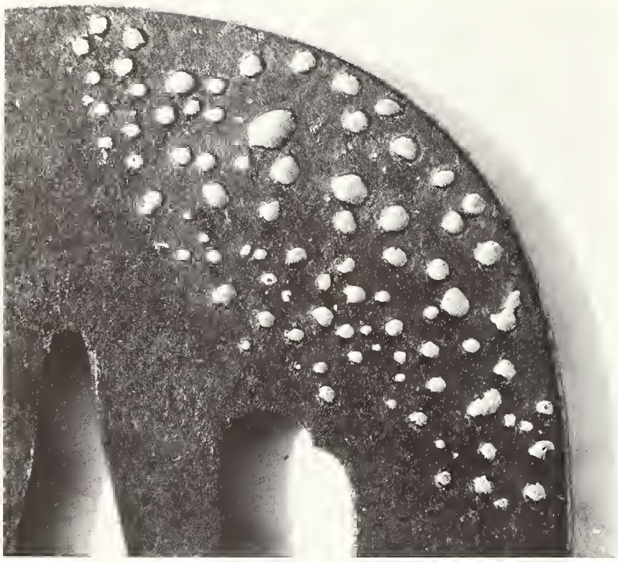

Fig. 35.—Iron tsuba with applied drops of metallic silver, *gama-hada* "toadskin" surface. ×5. Private collection.

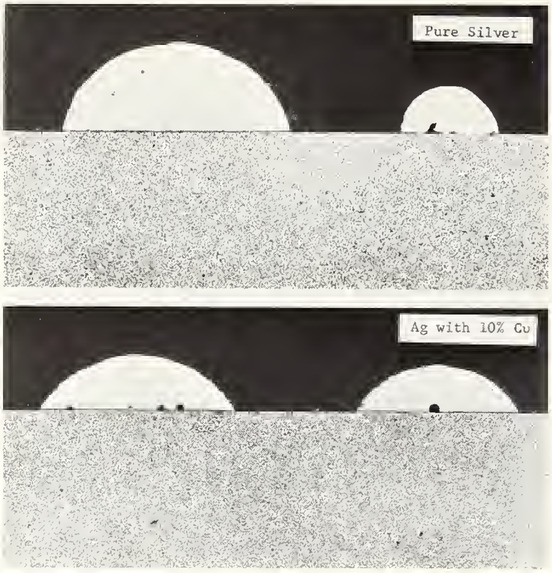

Fig. 36.—Cross sections of silver drops fused onto a surface of iron (mild steel). ×11. Note the smaller angle at which the drops join the iron surface when they contain copper.

An interesting variation is the use of silver in the effect called *gama-hada*, "toad-skin" surface. In this, convex drops of silver are attached to an iron surface to yield interesting contrasts of shape, texture and color (fig. 35). For rather subtle reasons dependent on the balance of interatomic forces at the interfaces between the iron, the silver, and the air, the molten metal does not spread out over the surface, but remains as drops with a well-defined angle of contact (fig. 36).

GILDING

Small golden details were often achieved by direct inlay of a high-karat gold alloy. Some of the gold areas in elaborate colored-metal inlay (*iroe*) appear to be made by direct mechanical application of gold sheet to a roughened copper-base alloy in a manner like *nunome* but with thicker layers of the precious metal, followed by extensive working of the surface. The wire inlay in some early iron tsuba was amalgam gilded.

An example of the gold spot inlay, *keshiire-zōgan* or *keshi-komi-zōgan*, used only on tsuba of copper-base alloys, is found on the reverse of our Number 3, by Hirochika (fig. 3b). A cross-section through one of the spots viewed at high magnification (figs. 37 and 38) shows a shallow cavity, produced by punching, which contains a soft, yellow metallic material. There is an extremely thin layer of compacted gold at the surface. That heating was necessary to produce this effect is shown not only in the recrystallization of the brass base metal in the region distorted by the punch, but also in the layer, about 6 microns thick, of a solid, etch-resistant alloy, a product of the diffusion reaction between the applied alloy and the brass. Beneath this is a region in which intergranular penetration has occurred. It is likely that the spots were made by applying

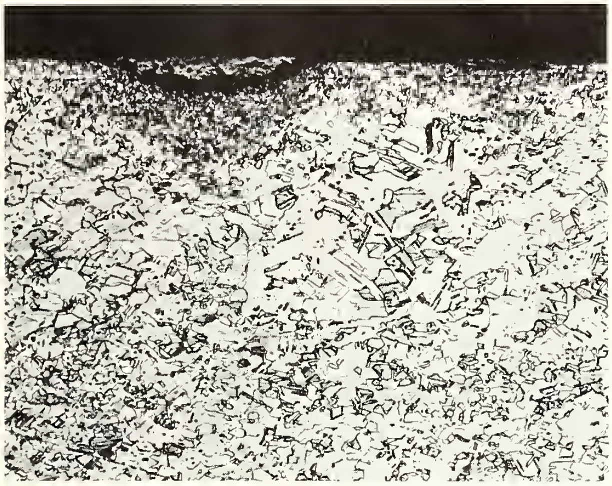

FIG. 37.—Tsuba no. 3. Cross section through two spots of gold in area of *keshiire-zōgan*. Etched, ×50. Note the fine recrystallized grain size beneath the depression produced by punching.

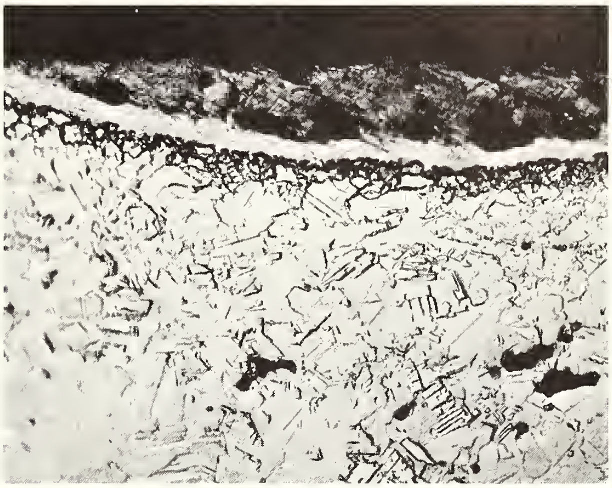

FIG. 38.—Detail at higher magnification of the gilded spot shown in Figure 37, ×500. Note the fringe of intergranular penetration, the reaction zone, and the soft metallic material which fills the cavity.

drops of gold amalgam in the prepared cavities, gently heating to evaporate the mercury, then compacting the residual gold and polishing the whole to a flat surface prior to patination. The electron microprobe (fig. 39) shows that the soft material comprising the main volume of the spot contains gold.[20] In other tsuba several different, tiny punches, round, rectangular, and irregular, were used in concert to prepare the ground for this process, often with spectacular effect.

Ogawa[21] mentions a technique of inlay, *suritsuke-zōgan*, in which fine lines are produced by the application of gold amalgam to a rough surface prepared as for *nunome-zōgan*.

The tsuba with designs of broken fans worked in gold against a black iron-like ground, first made by Hayashi Matashichi, are technically interesting. They are known as *horikomi-zōgan*, ragged-edge inlay. One of these (perhaps a copy, though bearing Hayashi's signature) is shown in Figure 40. As far as can be deduced from non-destructive examination, the areas that were to appear in gold had been left in low relief by carving away the ground, then, after etching or otherwise roughening the surface as for *nunome-zōgan*, a thick layer of gold was applied uniformly over both the depressed ground and relief areas. Following this a black lacquer was applied, leaving the relief features clear. On close inspection of Figure 40, several small areas can be seen where the lacquer has sealed off and exposed the matte surface of gold underneath. No iron is visible. The slightly irregular outline of the gold features, quite unlike the sharp edges of an inlaid piece, results from the relief and roughness of the iron, though the main effect of the tattered and torn fans results from the use of the chisel in shaping them.

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[20] No clear evidence of mercury was found in preliminary analysis by microprobe or emission spectroscopy. The above technical notes are based entirely on the microscopic features, especially the intergranular penetration, which is a feature that generally results from the penetration of a liquid metal.

[21] M. Ogawa in Compton, *et al.*, *Nippon-tō*, p. 77.

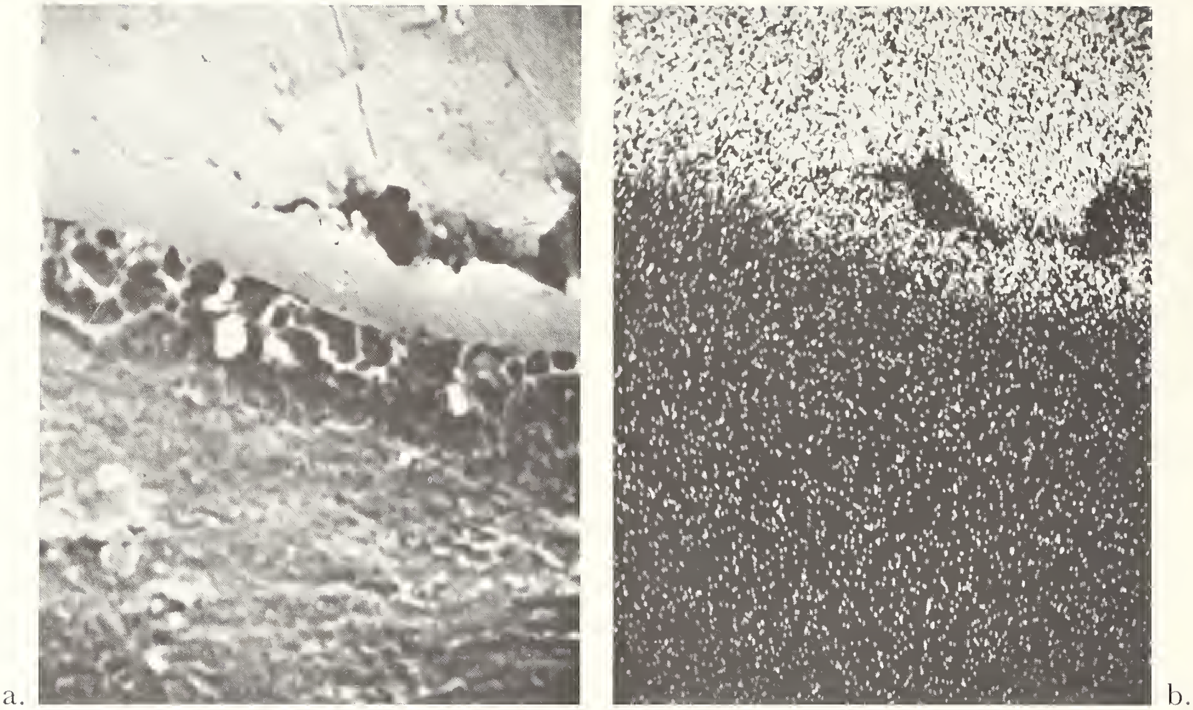

Fig. 39.—Photographs made on electron beam microprobe analyzer showing the distribution of gold in an area similar to Figure 38. a. Optical micrograph; b. Same area imaged with gold characteristic radiation. × 500.

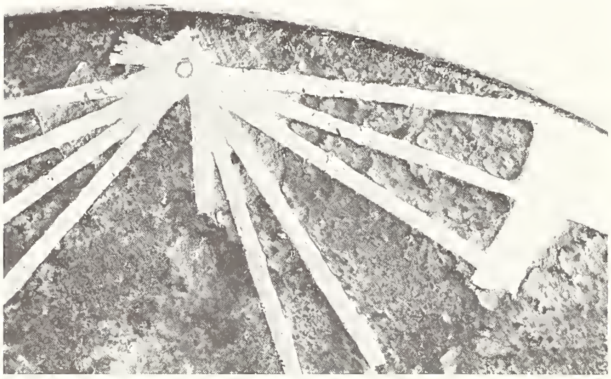

Fig. 40.—Tsuba with broken-fan design, signed "Hayashi Matashichi", but probably a copy. *Hotsure-zōgan*, "ragged-edge inlay". Detail, × 4. The surface, with design carved in low relief, had been thickly gilded all over, then covered with black lacquer (*tetsu-nuri*) in the sunken areas. The lacquer has flaked away, revealing the underlying gold, in an area near the center of the fan. MFA, Bigelow Collection, 13.1740.

GURI-BORI AND MOKUME

Figure 41 shows a detailed view of a typical *guri-bori* tsuba with its bold design of V-shaped grooves cut deeply into a stacked composite of alternating sheets of copper and *shakudō*. (The technique is analogous to that of the multi-layered *guri* lacquer, from which it takes its name.) Figure 42 is an edge view of the same tsuba, revealing four layers each of copper and *shakudō*, 0.27 mm thick, joined together to form a double layer of copper in the center with *shakudō* on both surfaces. There is very little solder visible between the layers; Figure 42 is of an area with an exceptional amount. The sheets when originally joined were thicker than at present. The subsequent hammering has produced a slight undulation of the interfaces and softened the geometric precision of the texture.

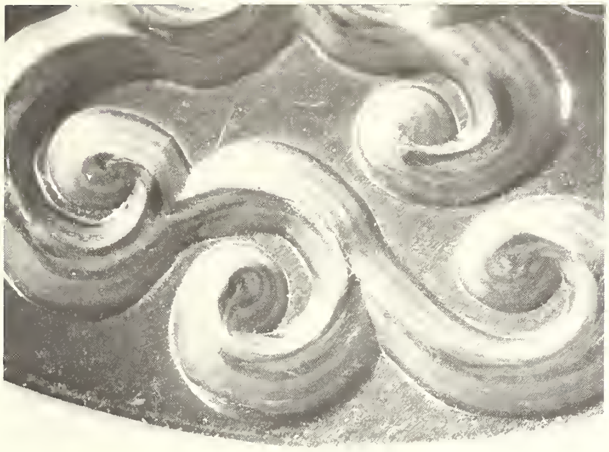

FIG. 41.—Tsuba with decoration in *guri-bori*. Detail, ×4. Laminations of *shakudo* and copper are exposed on the inclined sides of the deeply engraved cavity. MFA, Bigelow collection, 11.5363.

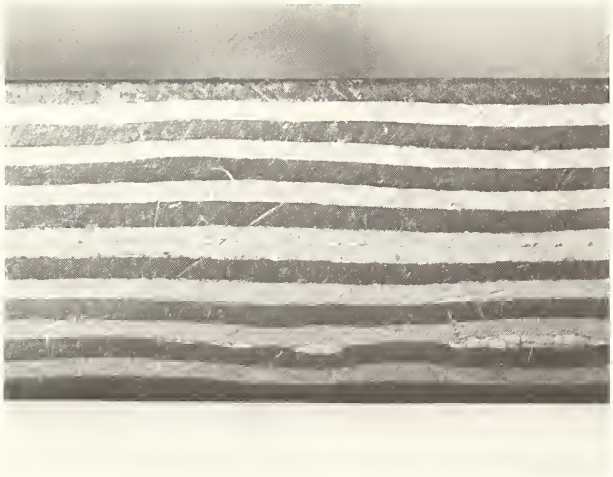

FIG. 42.—Edge view of the *guri-bori* tsuba shown in Figure 41. ×10. Note the double layer of copper in the center and the remnants of solder.

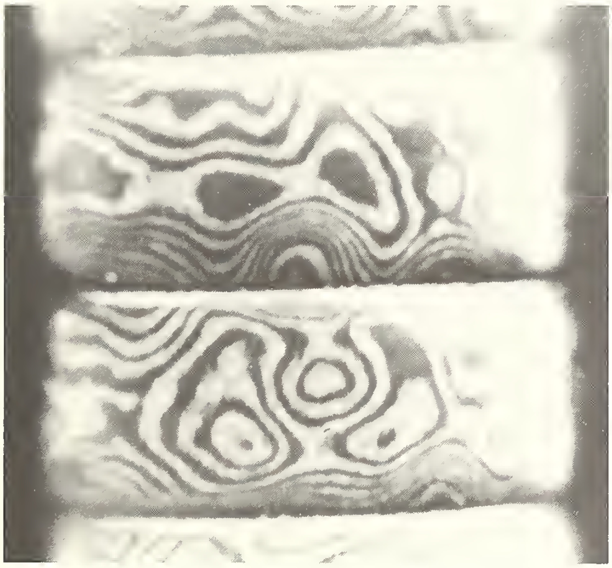

FIG. 43.—A *kozuka* with *mokume* surface. Detail, ×4.5.

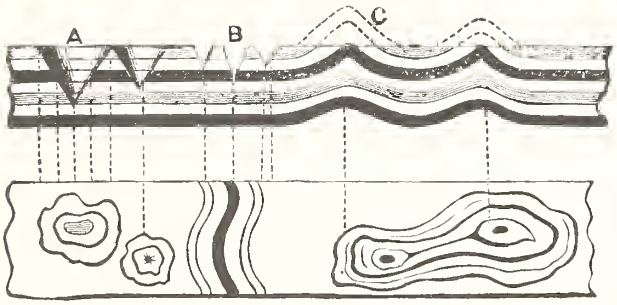

FIG. 44.—Drawing showing the preparation of *mokume* by cutting or contorting composite laminates of copper alloys selected to yield contrasting colors after patination. From Roberts-Austen, "Cantor lectures."

Non-ferrous metal *mokume* is also a composite formed of soldered metal sheets but the laminates are thinner than in *guri-bori* and are intentionally distorted into an irregular shape through which the smooth final surface is then cut. The texture arises from the interaction between localized deformation due to hammering and the smooth geometric surface achieved by cutting (fig. 43). The first account of Japanese metalworking methods to appear in English, by Pumpelly, described this technique.[22] Roberts-Austen[23] in 1888 published the first technical diagram (fig. 44).

Similar patterns may be achieved either by hammering slight projections and grinding

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[22] Pumpelly, *Notes on Japanese Alloys*.

[23] Roberts-Austen, *Cantor Lectures*.

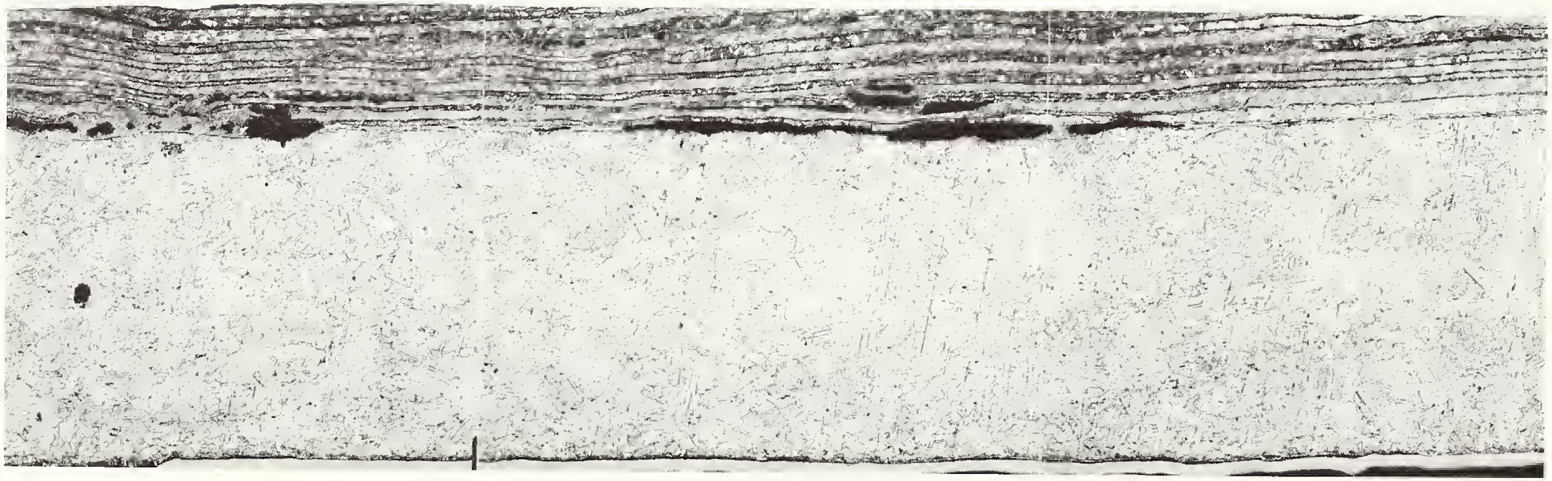

Fig. 45.—Cross section of a *fuchi* with a surface of non-ferrous metal *mokume*. Probably early nineteenth century. Etched, × 73. Note the layers of solder between the main laminae of copper and *shakudō*, and the way in which the lower layers rise to intersect the surface. (Photograph by Philip Wingert, courtesy of Dr. Michael Notis.)

through them or by cutting shallow cavities into the composite sheet and hammering it flat. In the final surface the widths of the laminae are magnified by the glancing angle of the cut (fig. 45), as discussed for ferrous *mokume*. The resulting pattern of irregular but never intersecting lines on the surface resembles the contour lines on a map of gently rolling, hilly terrain. Unlike *guri-bori* in which composite metal makes up the entire thickness of the piece, the textured metal in non-ferrous *mokume* work is often applied as a veneer, approximately 0.5 mm thick.

In non-ferrous metal *mokume*, the identity of the few laminates is usually preserved in simple patterns. The highly contrived cherry blossoms in the tsuba illustrated in Figure 46 were probably made from a composite of thin sheets having a thick sheet of *shakudō* as its outer layer; by local depression of the surface to a predetermined level with a flat-ended, petal-shaped punch and grinding the rest of the metal to this surface level, the blossoms would appear in solid *shakudō* with the desired outline. The wave-like pattern extending over the entire tsuba would

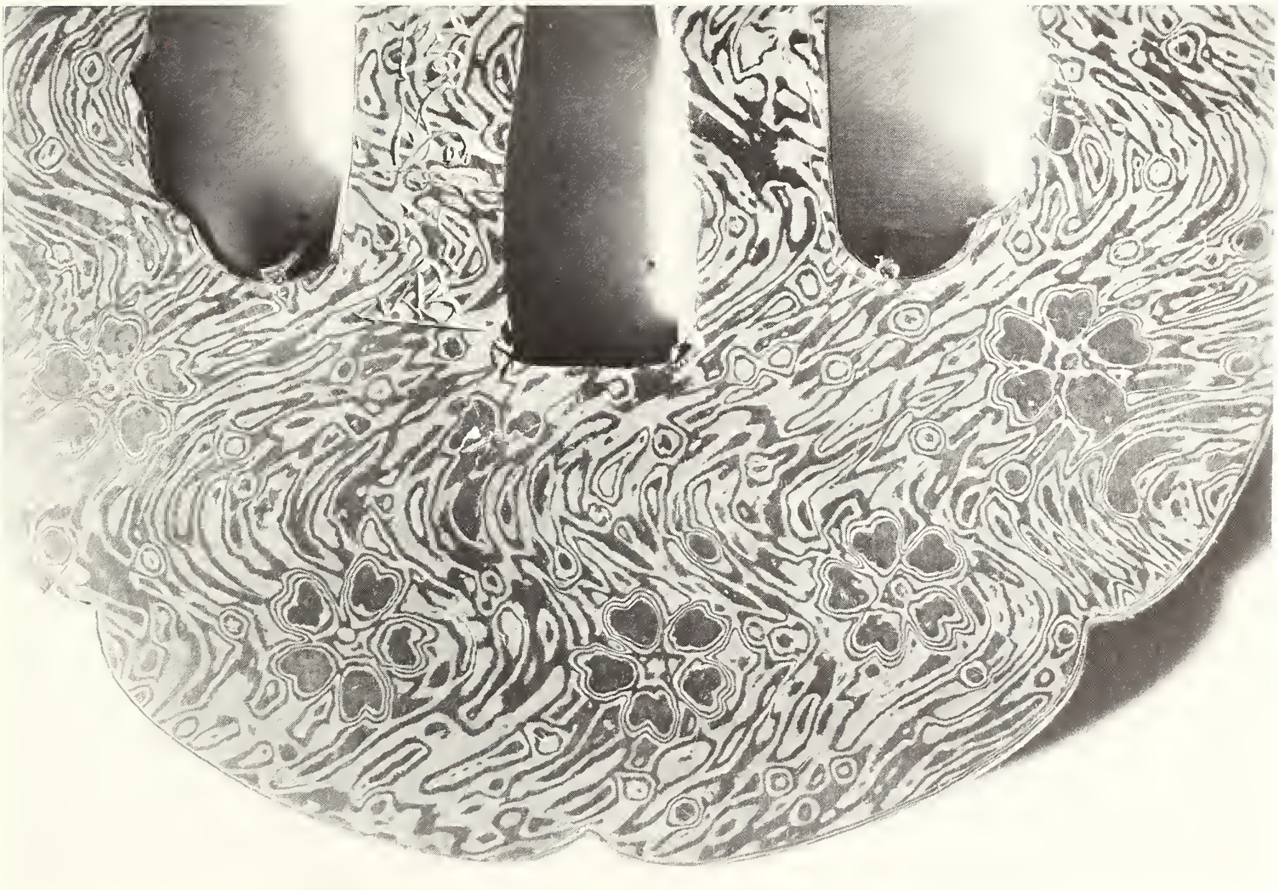

Fig. 46.—Tsuba in *mokume* composed of copper and *shakudō*, worked to depict cherry blossoms floating on the wind-rippled surface of a pond. Signed, "Takahashi Yogi", nineteenth century. Detail, ×2. MFA, Bigelow Collection, 11.12445.

require only gentle repoussé to produce undulations in three dimensions which could be ground down to a plane surface.

The *mokume* technique is being revived in modern Japan using laminations of copper, *shakudō*, and *kuromido* (a dark etching alloy of copper with small amounts of arsenic) joined without solder by solid-state diffusion welding under slight pressure.[24]

MECHANICALLY PRODUCED SURFACE TEXTURES

Innumerable types of punched, engraved and abraded surface textures on tsuba have been illustrated in the literature: the following discussion relates to only a few of them. Figures 47 and 48 are low magnification photographs of the popular *nanako-ji* ("fish-roe" surface), which is created using punches having ends about 0.3 mm in diameter with a hemispherical concavity, applied with incredible precision. In Figure 48, a *kozuka*

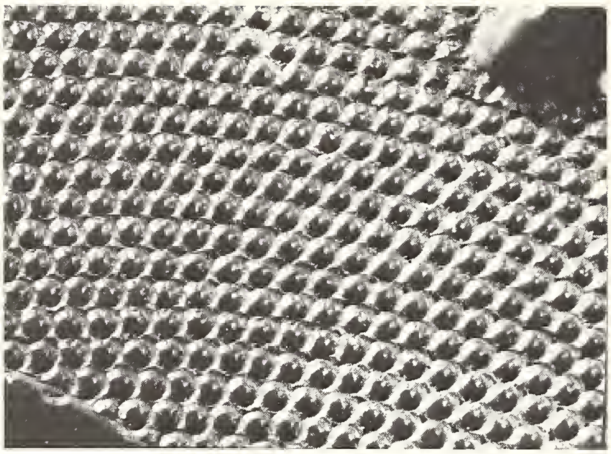

Fig. 47.—Tsuba in *shakudō*, detail showing surface texture called *nanako-ji*. × 10.5. Private collection.

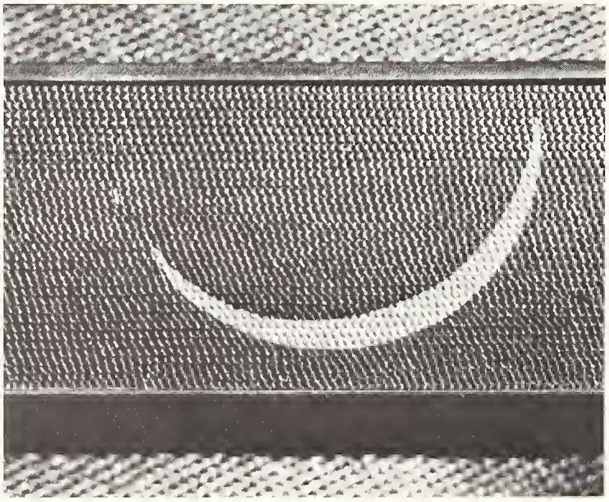

Fig. 48.—Detail of a *kozuka* by Kanō Natsuo, executed in *shakudō*, with fine *nanako-ji* extending over a gold moon inlaid in *hira-zōgan*. × 3. MFA.

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[24] H. S. Pijanowski and E. M. Pijanowski, ". . . Adaptations of the traditional Japanese Technique of Mokume-gane . . .", Pamphlet with separate pagination accompanying *Goldsmith's Journal*, vol. 3, no. 4 (August 1977). At a meeting of the Materials Research Society in November 1978 Michael Notis reported new studies of *mokume*. Examination of a number of samples indicated that two different bonding techniques have been used. In most cases the layers were bonded by solid-state diffusion as described by Pijanowski. However, in other cases, although Notis found little visible evidence of an intermediate layer of braze material, electron microprobe analysis revealed a concentration of silver diffusing away from the junction into both the *shakudō* and the copper. This suggests that a thin layer of silver had been applied to one or both of the surfaces before assembly, followed by heating above 780°C to produce by reaction a transient layer of liquid Cu-Ag eutectic, which, being thin, would quickly disappear into solid solution by diffusion. The measurements correspond to a pure silver layer only a few microns thick, which before the days of electroplating could have been applied by electrochemical replacement. Some uniform pressure would have been necessary to obtain contact over the entire surface, though liquid would accumulate and remain in occasional larger spaces as in the area shown in Figure 42. Except for the use of silver on copper in place of copper on gold, the mechanism is similar to that underlying the invisible soldering used by the Etruscan goldsmiths in their famous granulation technique.

(a small utility knife carried in a pocket of the scabbard) by Kanō Natsuo, note that the punching has been done on a smooth surface of *shakudō* in which a moonshaped inlay of gold had previously been inserted by *takazōgan.* The crystallographer will notice that these uniform rows of punch marks contain occasional mismatches analogous to the configurations called dislocations that occur in an extended crystal lattice.

The "stone-surface" texture *ishime-ji* has irregular roughness. Though in old iron tsuba it often resulted from heat scaling and corrosion, its intentional reproduction by the smith was often accomplished by the use of irregular punches or sometimes simply broken ones whose end had fractured in a coarsely crystalline or granular way. Although such punches were repeatedly used on the same surface, they were oriented randomly so that the viewer is usually unaware of the repetition in detail. Figure 49, which is not of a typical *ishime-ji*, shows well this effect of punch orientation.

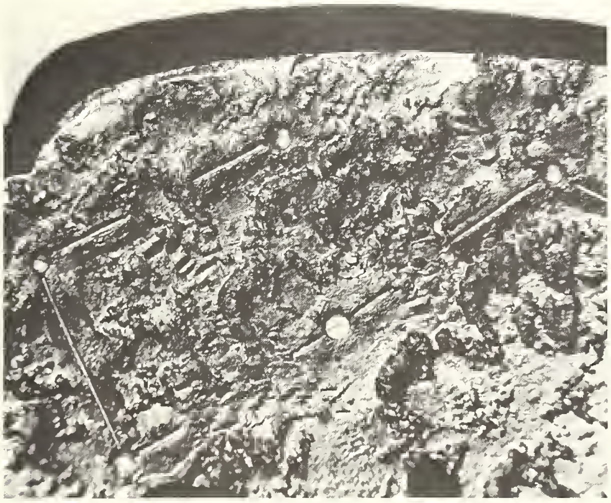

Fig. 49.—Iron tsuba with surface of rough texture produced by an irregular punch. ×4.3. Private collection.

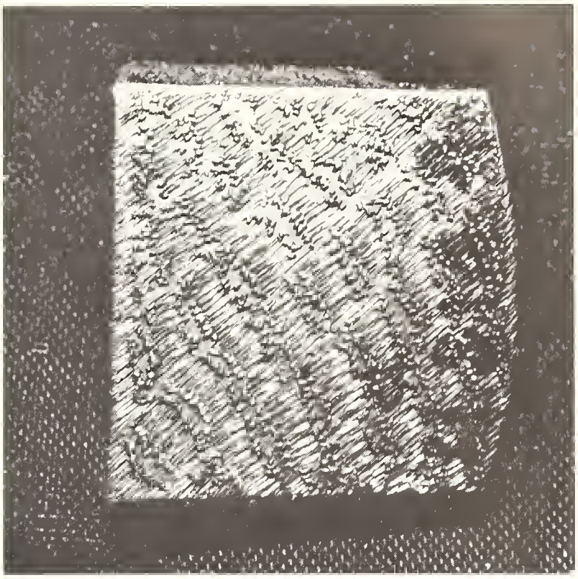

Fig. 50.—Gold *habaki* from a dagger, with surface decorated with *neko-gaki.* ×2.3. Note the turned-up chips of metal still remaining at the end of each engraved line. This effect is only possible with ductile metals.

Two effective engraving techniques are *nego-gaki* and the highly expressive *katakiri-bori.* In *neko-gaki* (fig. 50), the texture produced by parallel engraved lines is enhanced by allowing the chip of metal turned up by the engraving tool to remain attached at the end of the groove. *Katakiri-bori* (fig. 51) is a method of pictorial engraving in which lines of varying width are produced by using the graver at an angle, with one edge cutting vertically. The effect has a richness comparable to a line in an ink-brush painting.

The techniques of perforation used in the popular openwork tsuba known as *sukashi* tsuba involved great skill in design and control but little metallurgical ingenuity. Some tsuba smiths made finely cut, parallel-sided lines (*ito-sukashi*). These are sometimes described as resulting from a wide, more easily cut slit which is subsequently closed by

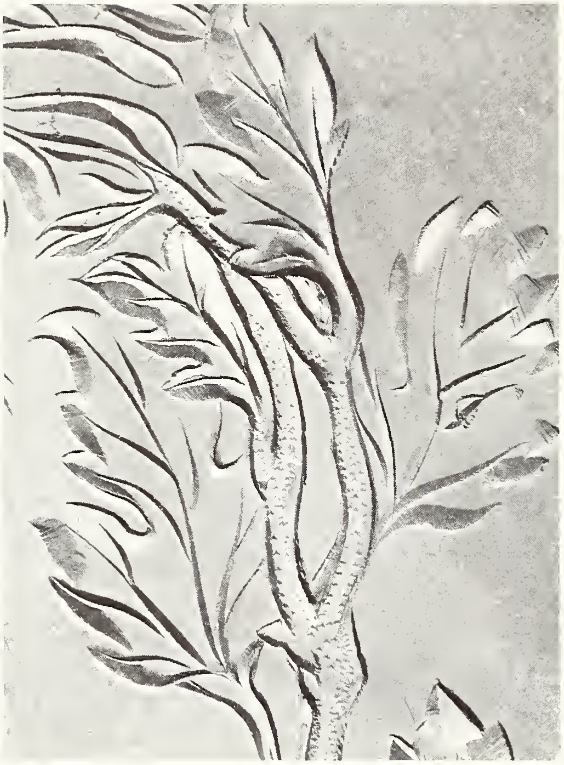

Fig. 51.—Tsuba of brass with design engraved in *katakiri-bori*, ×5. The expressive lines, of variable width, are cut with a graver, one side of which is vertical, the other strongly inclined. Faint crystalline texture is visible in the background. MFA 11.5379.

deformation of the adjacent metal. In one we have examined (fig. 52), the three lines (which are about 0.2 mm wide) in the body of the fish show no evidence of such an operation. The mystery lies mainly in the skill needed to make a sufficiently small starting hole and to guide the saw. One can suspect the use of an abrasive coated wire and a jig, external to the *tsuba*, in order to prevent rounding of the edges.

The Museum of Fine Arts, Boston, has an iron tsuba with a hexagonal pattern of straight lines, about 0.7 mm wide, cutting the metal almost through from both sides (fig. 53). The residual stubs are rounded and the tsuba was evidently made by the use of a flexible, abrasive-coated wire threaded to form a loop between adjacent pairs of holes and worked back and forth.

CRYSTALLINE TEXTURE REVEALED BY CHEMICAL ETCHING

The final treatment of Japanese metalwork consists of producing a patina by chemical attack. On *sentoku*, *shakudō*, and iron (excluding *mokume*) this is usually uniform over the whole surface and of a color dependent only on the composition of the metal and on the composition and application of the pickling solution. More subtle effects depending on the microcrystalline structure were often produced, such as the previously discussed surface qualities of *shibuichi* with its range of colors from olive brown to a matte silver. This effect depends on the duplex (two-phase) microstructure of the alloy as in Figures 15 and 16. However, textures originating in the crystallization of the metal can also be produced in single phase alloys. Both the dendrites that form during solidification of the casting and the approximately equiaxed grains that form during the annealing of deformed, work-hardened metal have been utilized.[25]

Figure 54 shows that the warm roughness of the surface of a tsuba bearing the signature of Hayashi Matashichi, although it resembles the "pearskin" (*nashi*) type of *ishime-ji*, actually has its origin not in punch marks but in the action of an etching reagent on tiny

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[25] See C. S. Smith, "Metallurgical Footnotes," for photomicrographs of typical structures.

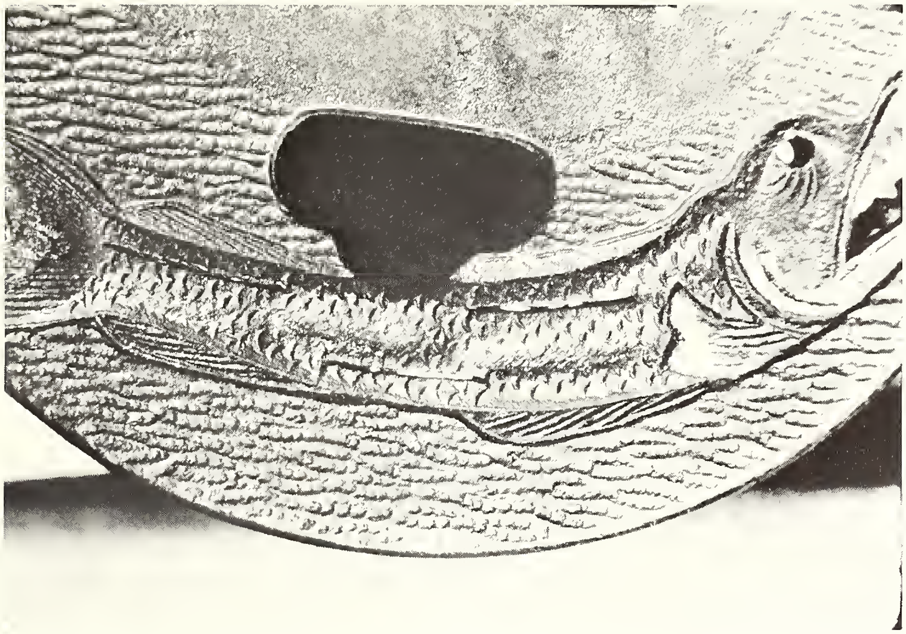

Fig. 52.—Tsuba signed "Ranzan Tsuneyuki", nineteenth century. Detail ×2.5. Note the three nearly straight lines in the body of the fish done in *ito-sukashi*, "thread-perforation", now partly blocked. Private collection.

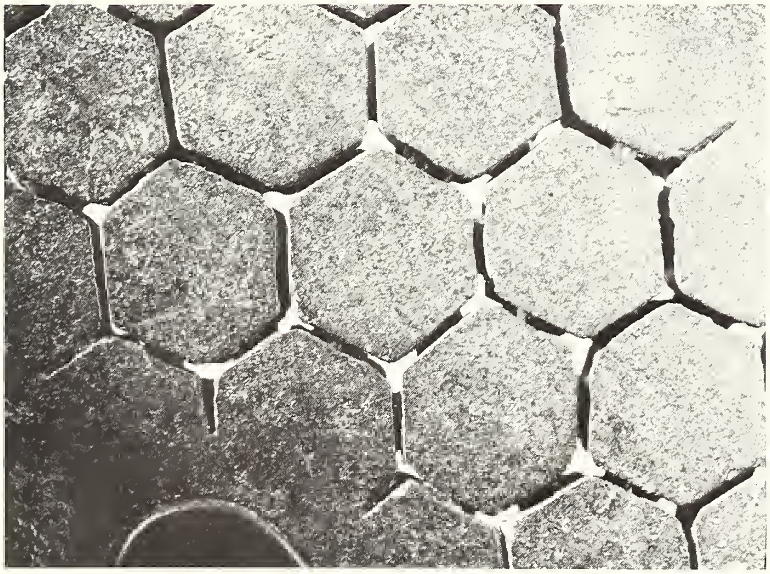

Fig. 53.—Iron tsuba with hexagonal network of finely cut lines, evidently made with an abrasive-coated wire moving between pairs of drilled holes. A small rounded stub of residual metal remains in the center of each cut. ×5. MFA, Bigelow Collection, 11.11858.

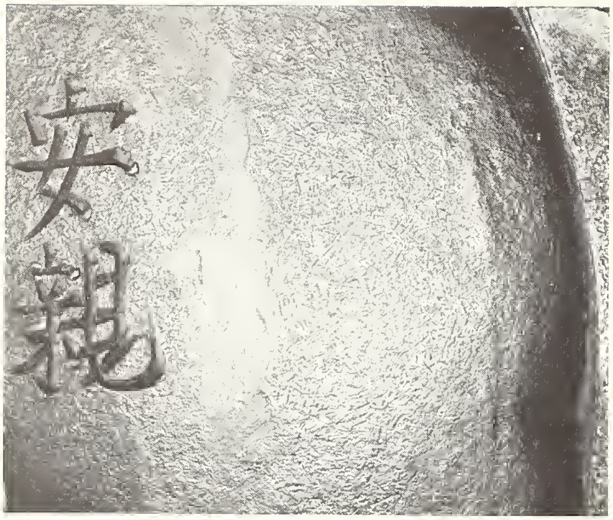

Fig. 54.—Tsuba in a brass-like alloy, signed by Hayashi Matashichi. This rough surface texture is clearly composed of small dendritic crystals, developed by etching, and slightly polished thereafter. Detail, ×4.5. MFA, Bigelow Collection, 13.1740. (A larger and more deeply etched dendritic structure on a tsuba surface by another smith is illustrated in Figure 42 of Smith, "Metallurgical Footnotes.")

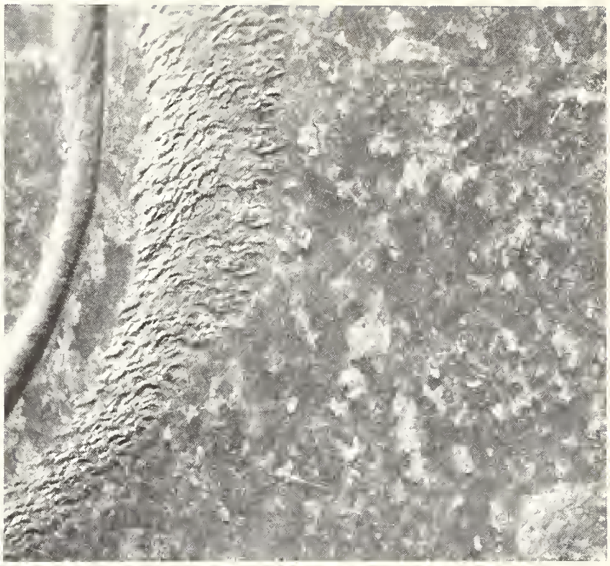

Fig. 55.—Brass tsuba, signed Takeaki, early nineteenth century. Detail of surface texture, showing etched equiaxed crystalline grains, a rough area produced by punching, and an engraved line. ×5. MFA 11.12414.

dendritic crystals. Figure 55 is a detail of an early nineteenth century tsuba by Takeaki in the Museum of Fine Arts, Boston, contrasting an engraved line and an area finely roughened by a punch against the main ground of just visible crystals, about 0.5–1.0 mm across.

Tsuba with visible textures originating in metallurgical treatment developed by etching are not uncommon although they are not recorded in either Japanese or European literature. The use of etching to show crystalline forms in metals became a central feature of the scientific study of metals in Europe in the latter half of the nineteenth century[26] although decorative applications were earlier.

PATINATION

Finally we come to discuss uniform patination, one of the most important aspects of Japanese metalwork, and we have very little to say regarding it. All the metallurgical operations including alloying, casting, forging, carving, inlay and engraving can be viewed as the preparation of a suitably shaped foundation for the patterns of color produced by chemical treatment. Except for the gold, and sometimes silver, none of the colors appearing on the surface of a tsuba are truly metallic, but rather result from thin layers of oxides, sulfides or other compounds produced by chemical reaction modifying and sometimes even obscuring the reflection of light from the surface of the metal. The skill by which the many different alloys are given their properly balanced colors by the same final patination treatment is admirable. Patina is the product of an interrupted early stage of corrosion which, if allowed to proceed, would disfigure and eventually destroy the object. Some of the richer colors arise from dispersion of colloidal particles within the main corrosion products. The patina on *shakudō* has colloidal particles of gold of such a size and dispersion that they totally absorb light, while arsenic warmly darkens the patina on some of the less pure copper pieces.

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[26] C. S. Smith, *A History of Metallography*

After being produced, the films of patina were often modified by polishing and gentle heating, sometimes after the application of lacquer or other organic materials, which enhance the color while delaying tarnish.

Our own attempts to produce patina have had limited success. Ingots of various compositions of *shakudō* and *shibuichi* were cast, sectioned, polished and pickled in solutions of the compositions published by Roberts-Austen,[27] Gowland,[28] and Wilson[29] consisting mainly of verdigris, copper sulfate, salt and water, as well as others containing vinegar and sulfur. The effect of these solutions on the *shibuichi* specimens was usually unpleasant, producing a dull grey surface. *Shakudō* with either 5% or 10% gold acquired a good patina with shades ranging from violet to black, depending on the number of picklings given to the specimen. The metallographer's bichromate etching solution also produced a lustrous black patina. It was noticed that the untouched original surface of the cast *shakudō* remained unaffected by treatment that gave a good black finish on adjacent areas that had been abrasively polished.

Much of the special quality of the surface of Japanese metal work, as compared with European finishes, arises from the meticulous preparation of the surface before chemical treatment. Produced by the use of a series of graded abrasives of diminishing particle size, the surfaces, though finely matte, are free from distortion even on a microscopic scale. This is why the *shibuichi* of Figure 15 reveals the distribution of silver with all the crispness of a metallographer's laboratory preparation. In contrast, European metalworkers generally finish the surfaces of their work by burnishing or buffing to give a superficial gloss of flowed metal with microcontours unrelated to the main shaping process and with defects exaggerated into pits or streaks.

The beauty of any work of art lies less in the materials and techniques that are used than in what is done with them. However, the photographs of the two sides of the *menuki* shown in Figure 56 are introduced as a reminder that the symbolism and aesthetic overtones could not exist without a technical underside.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Jan Fontein (Director of the Museum of Fine Arts, Boston) and Mr. Money Hickman who gave us access to the Museum's collection of tsuba and permitted us to remove samples from five of the mutilated tsuba in the Bigelow collection. Mr. W. J. Young (head of the research laboratory at the Museum until his retirement in 1976) provided much

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[27] Roberts-Austen, "Cantor Lectures."

[28] Gowland, "Metals and Metalworking."

[29] Wilson, "Silverwork."

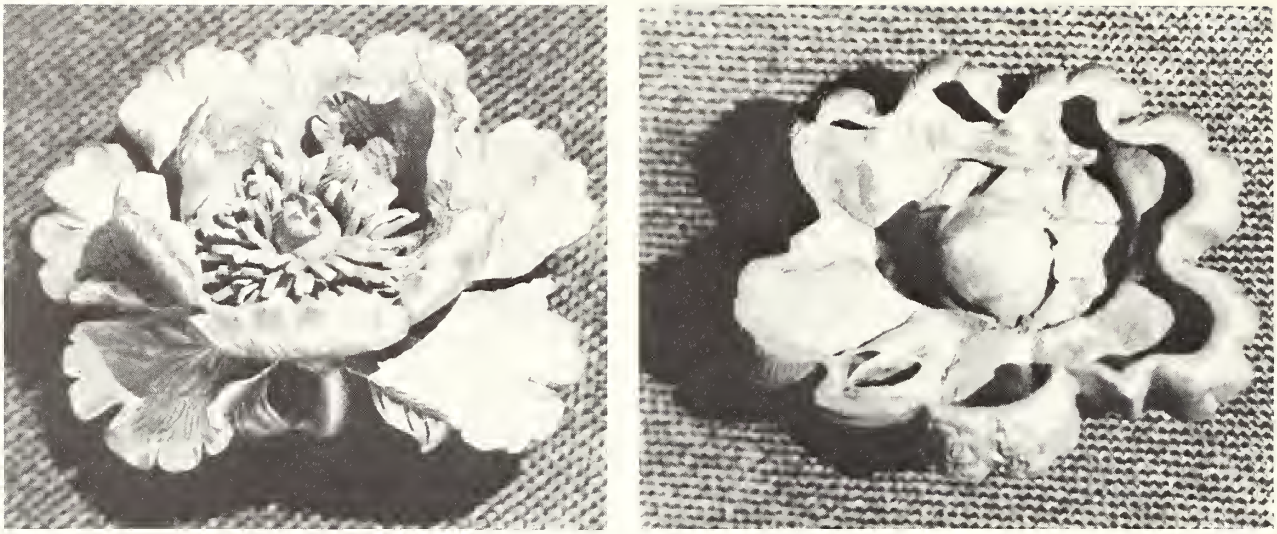

FIG. 56.—*Menuki* in the shape of a peony, a. front view, b. back view, signed "Norinaga", early nineteenth century. The entire flower was made from a single sheet of gold by the high-repoussé technique called *uchidashi*. The petals were first formed as protuberances by raising and repoussé work, then flattened and given a detailed shape and surface texture by chasing. The pistil and stamen are separate pieces. Some idea of the intricacy of the process can be gleaned from the nature of the folds visible from the back side (fig. 56b). Maximum diameter of the peony is 2.1 cm. MFA 11.5280.

useful advice and gave us access to photographic facilities; Ms. Florence Whitmore performed some of the spectrographic analyses. We are especially indebted to Mr. Morihiro Ogawa, of the Society for the Preservation of Japanese Art Swords, Tokyo. He helped immeasurably with discussions of tsuba in general and in detail, has read the manuscript of this paper, and has kindly checked our Japanese terminology. Photographic work was aided by a grant from the Wenner-Gren Foundation.

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